

Analytical Abstracts

A monthly publication
dealing with all branches
of analytical chemistry:
issued by the Society
for Analytical Chemistry

Volume 7
No. 2, Abstracts 335-847

February, 1960

Binding . . .

W. Heffer & Sons Ltd. announce that they are now able to BIND copies of ANALYTICAL ABSTRACTS, in an approved binding case, at a cost of 12/6 per volume. The 12 Parts for 1958 together with Index and remittance for 12/6 should be sent to

**W. HEFFER & SONS, LIMITED
HILLS ROAD, CAMBRIDGE**

IMPORTANT NOTICE TO SUBSCRIBERS (Other than Members of the Society)

The Subscription to *Analytical Abstracts*, inclusive of Index, is £5 per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes is £8 8s. per annum.

The price of single copies of *Analytical Abstracts*, including back numbers, is 10s. 6d. post free.

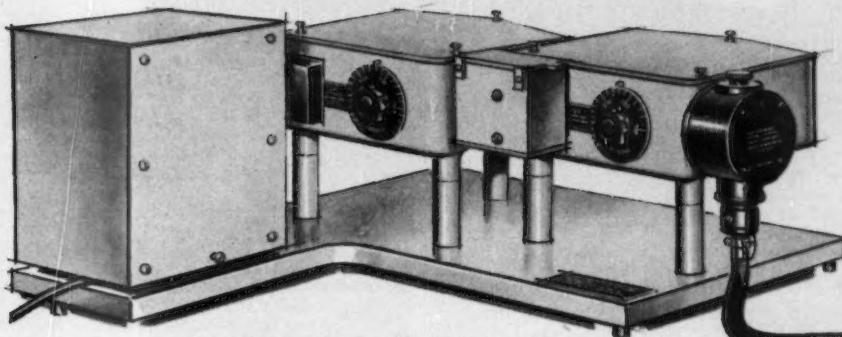
Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost is £5 7s. 6d. per annum, exclusive of Index.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

ANALYTICAL ABSTRACTS

unequalled for

VERSATILITY



Farrand

SPECTROFLUOROMETER

Versatile instrument for photo-fluorometric assay, identification and analysis of chemical constituents in the Ultraviolet, Visible and Infrared. Measurements are much more dis-

criminating than obtained through colorimetric or spectrophotometric methods. Can be used for micro or macro volumes. Models for manual, oscilloscope or chart recording available.

*Technical data available on request
Specify Bulletin No. 820AA*

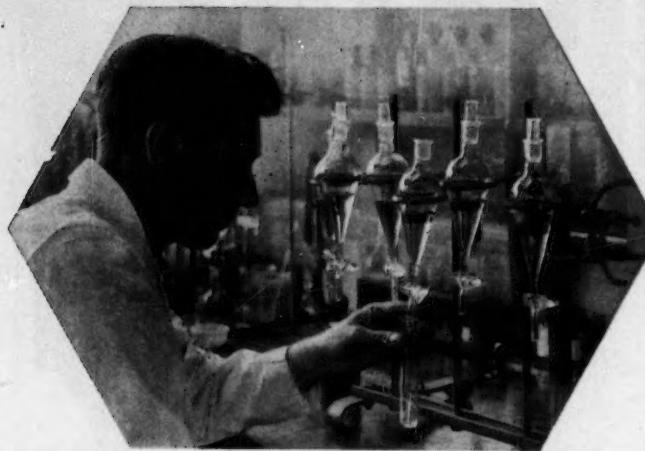
FARRAND OPTICAL CO., INC.

BRONX BLVD. AND EAST 238th STREET • NEW YORK 70, N. Y.

Engineering, Research, Development, Design and Manufacture of Precision Optics, Electronic and Scientific Instruments

Incidental information

No. 13



*Items of
interest
from our
laboratory
notebooks*

- Most analysts know about 1:10-phenanthroline and many use it for iron determinations. Not so many people seem to know that 4:7-diphenyl-1:10-phenanthroline is twice as sensitive as 1:10-phenanthroline in the colorimetric determination of iron. There are several papers on the subject but the latest is *Analyst*, 1958, 83, 80. The reagent is also called **Bathophenanthroline**, and we make it.
- Then, again the substitution of methyl groups in the 2:9 positions has the interesting effect of making the reagent insensitive to iron and we then have a selective and sensitive reagent for copper (see *Anal. Chem.*, 1956, 28, 1158). Hopkin & Williams make 2:9-dimethyl-
- 1:10-phenanthroline (sometimes called **Neocuproin**).
- One does not think of sulphate as a radical one can determine absorptiometrically, but this is now possible for low concentrations. **Barium chloranilate** is the reagent and there are two papers on the subject—*Anal. Chem.*, 1957, 29, 281 and *Anal. Chem.*, 1958, 30, 202. Hopkin & Williams make it.
- Hopkin & Williams Ltd. were also early off the mark with supplies of the remarkable new colour-producing reagent for fluoride ions, **3-aminomethylalizarin-NN-diacetic acid**, described by Belcher, Leonard and West (*Talanta*, 1959, 2, 92.) This important reagent is already available from stock.



FINE CHEMICALS
for research and analysis

HOPKIN & WILLIAMS LTD., CHADWELL HEATH, ESSEX, ENGLAND
London, Manchester, Glasgow.

Agents throughout U.K. and all over the world.
TAS/HW.6

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

335. Second Conference—Analytical chemistry in nuclear reactor technology. Part I. Specific applications of diverse methods of chemical analysis. Gatlinburg, Tenn., 1958. U.S. Atomic Energy Comm., Rep. TID-7568 (Pt. I), 305 pp.—The following communications are included. Analysis of reactor alloys, R. W. Bane, pp. 3–8. The spectrophotometric determination of zirconium, molybdenum, ruthenium, palladium and cerium in uranium “fission” alloys, R. P. Larsen and L. E. Ross, pp. 9–19. Rapid analysis of dissolved gas in high-pressure coolant water, E. L. Shirley, pp. 20–23. Analysis in reactor research at Harwell, G. W. C. Milner, pp. 24–35. Chemical control of pressurised-water test loops and autoclaves, B. D. La Mont, J. V. Derby, C. A. Meinz and J. D. Johnson, pp. 36–49. Analytical requirements of the Lockheed critical experiment reactor, of the radiation effects reactor and of the radioactive waste disposal system, J. H. Edgerton, pp. 50–74. The volumetric determination of microgram quantities of boron, Hisashi Kubota, pp. 77–86. Colorimetric determination of boron: a study of the variables involved in the quinalizarin method, J. E. Kelly, pp. 87–95. Analytical applications of ethylenediaminetetraacetic acid and its salts, T. H. Whitehead, pp. 96–100. Determination of deuterium, oxygen and nitrogen in helium by gas chromatography, D. L. West, pp. 101–104. Spectrophotometric determination of cerium in fluoride salts, J. C. White and R. F. Apple, pp. 105–112. Application of the lead reductor to the determination of uranium, B. A. Swinehart, pp. 117–123. Colorimetric uranium determination with arsenazo, J. S. Fritz and M. J. Richard, pp. 124–134. Determination of microgram concentrations of zirconium in organic and aqueous solutions containing uranium, P. G. Laux and E. A. Brown, pp. 135–139. Determination of corrosion products and anions in aqueous thorium-uranium slurries, B. D. La Mont and J. D. Johnson, pp. 140–149. Determination of copper, molybdenum, silver and palladium in aqueous thorium-uranium slurries, C. A. Meinz and B. D. La Mont, pp. 150–156. Determination of aluminium, zirconium, molybdenum, uranium and titanium in thorium oxide slurries, O. Menis, T. C. Rains, D. L. Manning, G. Goldstein and I. B. Rubin, pp. 157–168. Characterisation of uranic oxide by a reflectivity technique, B. A. Swinehart, pp. 183–193. Flame-photometric determination of sodium and calcium in uranium ore concentrates, L. A. Ferguson, pp. 197–204. Direct flame-photometric method for the determination of micro quantities of alkali metals in concentrated solutions of uranyl nitrate, W. G. Ellis and E. A. Brown, pp. 205–212. Determination of small amounts of magnesium in uranium with the flame photometer, C. H. McBride

and W. A. Ziegler, pp. 213–223. Indirect assay of uranium tetrafluoride by the polarographic determination of uranyl fluoride, T. J. Kneip and J. D. Dowdy, pp. 224–232. Determination of individual rare earths in product uranium, M. G. Atwell, C. E. Pepper and G. L. Stukenbrocker, pp. 243–252. Spectrographic determination of impurities in uranium–molybdenum alloys, E. R. Barker, C. E. Pepper and G. L. Stukenbrocker, pp. 253–257. A fluorescent X-ray spectrographic method of analysing titanium–niobium alloys, D. E. Fornwalt and J. Komisarek, pp. 258–264. Spectrographic determination of trace impurities in niobium, D. E. Fornwalt and M. K. Healy, pp. 279–286. The spectrographic excitation of iron with iron-59, M. G. Atwell, C. E. Pepper and G. L. Stukenbrocker, pp. 287–293.

336. X-ray fluorescence analysis. A review. F. Brown (Res. Dept., I.C.I. Ltd., Billingham Div., Co. Durham, England). *Analyst*, 1959, **84**, 344–355.—The development of X-ray spectra and X-ray spectrometry is reviewed, with descriptions of the equipment used for the application to qual. and quant. analysis of measurements of the intensity and wavelength of the secondary or fluorescence radiation. The method can be applied to the determination of the elements from Na (11) to U (92) in powder, metal or liquid samples with coeff. of variation of $\leq 1\%$ in the concn. range 5 to 100%, and 5% in the range 0.1 to 1%. In some instances, determinations of a few p.p.m. can be made. The method is independent of the state of combination of the element and, although preparation of the specimen may be necessary, it is not destroyed. (77 references.)

A. O. JONES

337. Enzymatic methods in analytical chemistry. T. M. Devlin (Merck Inst., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 977–980.—Enzymatic techniques are discussed with regard to their advantages and limitations. The major advantage of an enzymatic assay is its specificity, which permits the measurement of only one member of a homologous group of compounds or one optical isomer. The types of assay include enzymatic catalysis of a reaction in which a change in the substrate or the reaction products is easily determined, and the measurement of the rate, or the activation or inhibition of an enzymatic reaction. (24 references.)

G. P. COOK

338. Fusible extraction reagents in analytical chemistry. V. I. Kuznetsov and I. V. Seryakova (Vernadsky Inst. of Geochem. and Anal. Chem. Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1959, **14** (2), 161–166.—Solid, easily melted extraction reagents simplify extractive separations of elements since they allow extractions to be carried out in simple flasks or test-tubes without separating-funnels. Several such reagents are proposed which permit the extraction of elements from acid soln. (a mixture of HCl and H_2SO_4) in the range 0.1 to 18 N.

1-Naphthylamine or mixtures of dimethylaniline or *o*-chloroaniline with paraffin wax are suitable for extraction from slightly acid soln.; an extraction of Cd with these reagents is described. Mixtures of oxygen-containing solvents (e.g., ketones) with small quantities of paraffin wax are suitable for use with acid soln. >0.1*N*; an extraction of Fe with several such reagents and paraffin wax is described. All the reagent mixtures contain about 25% of paraffin wax.

K. R. C.

339. Thenoxytrifluoroacetone as a colorimetric reagent. Anil K. De and Shridap M. Khopkar (Dept. of Chem., Jadavpur Univ., Calcutta, India). *Chem. & Ind.*, 1959, (26), 854.—The colorimetric reactions of the thenoxytrifluoroacetone in benzene with weak acid soln. of UO_4^{2-} (Khopkar and De, *Anal. Abstr.*, 1959, **6**, 2950), Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} , Cr^{3+} and Ce^{4+} have been studied. For the red complex with Fe^{III} , Beer's law is followed at 460 m μ in the range from 1 to 12 μ g of Fe per ml; the pH should lie between 2 and 3. For the green complex with Cu^{II} , Beer's law is obeyed at 430 m μ in the range from 10 to 100 μ g of Cu per ml; extraction is quant. when the pH is >2. Citrate, tartrate and CN^- interfere with both reactions.

P. D. PARR-RICHARD

340. *o*-Carboxyphenylazo-1:8-dihydroxynaphthalene-3:6-disulphonic acid (sodium salt) as an analytical reagent. A. K. Majumdar and C. P. Savariar (Jadavpur Univ., Calcutta, India). *Naturwissenschaften*, 1959, **46** (9), 323-324 (in English).—The reagent is prepared by diazotising antranilic acid and coupling with chromotropic acid. It forms a blue-violet complex with Th (1:2), with an absorption max. at 590 m μ , and a red-violet complex with Zr (1:1), with absorption max. at 580 m μ , and may be used as an indicator in the complexometric titrations of Th at pH 2 to 3.6 or of Zr at pH 1.4 to 2.5.

A. R. ROGERS

341. Universal buffer based on tetramethylammonium hydroxide. F. Cappellini (Ist. Chim. "G. Ciamician," Univ. Bologna, Italy). *Boll. Sci. Fac. Chim. Bologna*, 1958, **16** (4), 103-109.—To prepare a buffer soln. of the Britton and Robinson type, without alkali-metal ions, the use of tetramethylammonium hydroxide in addition to the usual acid components is proposed. This buffer soln. is very suitable for polarography, as reductions at the dropping mercury electrode are obtained at values beyond -2 V.

L. ZANONI

342. Magnetometric titration: a new method of chemical analysis. M. S. Blackie and V. Gold (King's College, Univ. of London). *Nature*, 1959, **183**, 1804.—The addition of paramagnetic solutes to H_2O greatly reduces the nuclear spin-lattice relaxation time (t_1) of solvent protons, according to the equation $(t_1^{-1} - t_0^{-1}) = \alpha \mu N C$, where t_1 and t_0 are relaxation times in the presence and the absence of solute, α is a proportionality constant, whilst C and μN are the concn. and the effective paramagnetic moment of the solute. When the addition of a complexing agent to a soln. containing a paramagnetic ion (M) causes the formation of a new, stable complex ion of different μN , the concn. of M can be determined with a low-resolution nuclear magnetic-resonance spectrometer. In this way, an ammoniacal soln. of $Ni(CN)_4^{2-}$ can be titrated with a standard soln. of KCN; the two end-points obtained correspond to the formation of stable

$Ni(CN)_4^{2-}$ and $Ni(CN)_6^{4-}$. A sample vol. of ≈ 0.25 ml and Ni^{2+} concn. of 0.01 to 0.1*M* are convenient.

W. J. BAKER

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

343. Identification of certain anions and cations in mixtures by means of the formation of coloured (ring) products on agar gel. B. D. Jain and S. P. Singhal (Dept. of Chem., Delhi Univ., India). *J. Chromatography*, 1959, **2** (3), 324-325.—A soln. containing the anions or cations is placed at the centre of a film of 1% agar gel supported on a glass plate. The agar gel contains a detecting reagent in a concn. of ≈ 0.01 *N*. After 2 to 4 hr., coloured rings are formed for the various ions, e.g., with a soln. containing S^- and I^- on a gel containing $HgCl_2$, a black inner ring is formed due to S^- and an orange outer ring due to I^- . The relative positions of the coloured rings depend on the solubility of the products obtained, the less soluble product forming the inner ring. Results are tabulated for 13 mixtures. A gel containing Ag_2CrO_4 can be used for the detection of halide and other anions. The preparation of the gels is described. The method may be used, with modification, for colorimetric determinations, and also for measuring the comparative solubility of insoluble substances.

S. M. MARSH

344. Behaviour of elements in trace amounts. A. K. Lavruchina (Inst. Geochem. and Anal. Chem., Acad. Sci., Moscow, SSSR). *Chem. Listy*, 1959, **53** (5), 465-480.—The results of experiments on the behaviour of ultra-micro amounts of elements during precipitation, extraction, electrolysis, distillation and chromatographic separation on ion exchangers are described. The elements used were ^{210}Bi , ^{131}I , ^{81}Y , ^{141}Ce , ^{142}Ce , ^{144}Ce , ^{59}Fe , ^{32}P , ^{76}As , ^{60}Co , ^{124}Sb , ^{65}Zn and ^{147}Nd , and their activities were measured with a statistical error of $> \pm 5\%$. It is stated that the behaviour of elements on the ultra-micro scale is often similar to that on the macro-scale, e.g., in the formation of co-ppt. of radio-isotopes with ppt. of the macro component (e.g., hydroxides). A characteristic shift of the dissociation equilibrium between the complex compound and simple ions in the direction of the complex form has been observed on the ultra-micro scale. This may cause an increase in the rate of elution of some elements during chromatographic separation on ion exchangers, an increase in the partition coefficient on extraction with organic solvents and a shift of chemical potential during the electrolysis of these elements.

J. ŽÝKA

345. Extraction of metals in the form of complexes by organic reagents. J. Starý (Dept. Nucl. Chem., Charles' Univ., Prague). *Chem. Listy*, 1959, **53** (5), 556-576.—The theoretical basis and practical possibilities are considered under four main heads: (i) the determination of the composition of the complexes; (ii) the determination of the stability constants of the complexes; (iii) the theory of the extraction of metals in the form of complexes with organic reagents, and (iv) analytical applications of the extraction method. (183 references.)

J. ŽÝKA

346. Extraction of transition metal-thiosulphate complexes. M. Ziegler (Univ., Göttingen). *Naturwissenschaften*, 1959, **46** (10), 353-354.—Some elements (e.g., Pd, Ag, Pb, V and U) form complexes in aq. soln. with $\text{Na}_2\text{S}_2\text{O}_3$ which, after the addition of amines or substituted ammonium salts, can be extracted with organic solvents. A list of suitable extracting solvents is given. G. BURGER

347. Precipitation of complex ions of the transition metals with water-soluble plastics. M. Ziegler (Univ., Göttingen, Germany). *Z. anal. Chem.*, 1959, **168** (1), 29-30.—Cationic resins of the urea-formaldehyde type, with a low degree of polymerisation, react with complex ions of the transition metals and form difficultly soluble precipitates. The precipitation reactions of the iodide, thiocyanate and azide complexes of Co^{3+} , UO_2^{2+} , Pd^{2+} , Cu^{2+} , Fe^{2+} , Bi^{2+} , Sb^{2+} and Au^{3+} with Lyofix SE, conc., are tabulated. S. M. MARSH

348. Quantitative inorganic chromatography. IV. Separation and determination of some heavy metals in admixture with lead. F. H. Pollard, J. F. W. McOmie and G. Nickless (Dept. of Phys. and Inorg. Chem., Univ., Bristol, England). *J. Chromatography*, 1959, **2** (3), 284-295.—The method is particularly applicable to the determination of small amounts of Cu, Fe, Cd, Zn and Bi in lead. An aq. soln. of the metal nitrates is applied to twin paper strips which have been pre-treated by acid washing for six days, and eluted with solvent A [50 ml of diethyl ether, 30 ml of methanol, 20 ml of water and 2 ml of HNO_3 (1:42)]. When Bi is present, elution must be carried out with solvent B [50 ml of diethyl ether, 30 ml of methanol, 22 ml of water and 4 ml of HNO_3]. The indicator sprays used to detect Ti, Ag, Pb, Zn, Cd, Cu, Co, Ni, Mn, Fe, Bi, U and Hg are tabulated. The metals are removed from the strip by elution with acid at high temp. by a prescribed procedure. Cadmium, Cu, Fe and Zn are separated by an anion-exchange method with a column packed with Amberlite IRA-400 resin, and eluting successively with 3 M HCl (for Cu, Ni, Co and Mn), 0.1 M HCl (Fe^{2+}), M NaOH containing 20 g of NaCl per litre (Zn) and finally with M HNO_3 (Cd). The metal contents of the eluates are determined spectrophotometrically. Results obtained for synthetic mixtures are tabulated. S. M. MARSH

349. Separations of cations on silica gel columns. H. W. Kohlschütter and H. Getrost (Tech. High School, Darmstadt, Germany). *Z. anal. Chem.*, 1959, **167** (4), 264-268.—Separation of cations on silica gel columns is facilitated by buffering the column at pH 5.7 (10% ammonium acetate-acetic acid), thus suppressing degradation of the adsorbed aquo-complexes. For a column 80 cm high and 1.2 cm in diameter, holding 50 g of silica gel, the throughput was 2 ml per min. Quant. separation is possible of pairs of ions comprising Al or Fe^{III} on the one hand and Ca, Ba, Mg, Ni, Cu, Mn^{II} , Zn or Fe^{II} on the other; Al and Be cannot be separated. J. P. STERN

350. Methods for the analysis of extracted inorganic compounds. Use of the Job method of continuous variation and conductimetric titration. H. Specker and E. Jackwerth (Inst. f. Spectrochem. u. angew. Spectroskopie, Dortmund). *Z. anal. Chem.*, 1959, **167** (6), 416-423.—The Job principle of continuous concentration variation modified for application to extraction reactions, and the method of "conductimetric extraction titration," in which

the conductivity of the organic phase is plotted against the vol. of titrant added to the aq. phase, are shown to have the same theoretical foundation. This has been worked out on the extraction of $\text{Fe}(\text{SCN})_6$, InI_3 and HgI_2 with cyclohexanone, and these cases are explained. E. G. CUMMINS

351. Rapid determination of tin, copper, lead, iron and nickel in brass and bronze. H. Wiedmann. *Metall.*, 1958, **12**, 1005-1007.—Procedures are described for the routine analysis of copper alloys for the elements named. Tin is determined volumetrically by titration with iodine soln. after dissolution of 1 g of sample in HCl and H_2O_2 and reduction of Sn by boiling with HgCl_2 and $\text{H}_4\text{P}_2\text{O}_7$; Cu by the standard iodide method; Fe photometrically with sulphonosalicylic acid; Ni photometrically after extraction of the ppt. obtained with dimethylglyoxime into CHCl_3 ; Pb by titration with EDTA (disodium salt) in the presence of aq. NH_3 , tartrate, triethanolamine, CN^- , and the Mg salt of EDTA, with Eriochrome black T as indicator. Eight results on each of two samples are given for each determination, showing good agreement with the accepted values. T. R. ANDREW

352. Photometric determination of small amounts of copper, bismuth, antimony and tin in metals and alloys, with sodium tetramethylenedithiocarbamate. E. Kovács and H. Guyer (Georg Fischer A.-G., Schaffhausen). *Chimia*, 1959, **13** (5), 164-165.—Sodium tetramethylenedithiocarbamate is suggested as a reagent for the metals named. The metal complexes are selectively extracted by CHCl_3 , or CCl_4 at definite (unspecified) pH values, and the extracts can be measured directly. Minute amounts of Bi (0.001% and less) can be extracted from iron and steel soln. with isobutyl methyl ketone, and similar concn. of Sb and Sn after a Blumenthal extraction in HClO_4 soln. Beer's law is followed under the following conditions—Bi at 365 μm up to 300 μg in CHCl_3 or CCl_4 ; Cu at 440 μm up to 60 μg in CHCl_3 or CCl_4 ; Sb at 365 μm up to 400 μg in CHCl_3 ; Sn at 390 μm up to 600 μg in CHCl_3 (1-cm cells). The reproducibility is $\approx \pm 5\%$ at higher concn. and $\pm 10\%$ at lower ones. H. M.

353. Quantitative determination of some noble metals by atomic-absorption spectroscopy. R. Lockyer and G. E. Hames (Hilger & Watts Ltd., 98 St. Pancras Way, London). *Analyst*, 1959, **84**, 385-387.—The determination of Ag, Au, Pt, Rh and Pd in concn. down to 1 p.p.m. in soln. is described. The spectrophotometer (a standard Uvispek H700 fitted with a Hilger H909 atomic-absorption attachment) is set to zero with distilled water sprayed into the flame. When the soln. of the metal is sprayed into the flame the signal traversing the flame from the hollow-cathode lamp is reduced by absorption in the flame, and the reduction is conveniently expressed as the extinction read directly from the spectrophotometer and referred to a calibration graph for the particular metal. Inter-element interferences are absent even when large amounts of Pb and Fe are present. With gold soln., precautions are necessary to prevent reduction to the metal, either by incompletely oxidised Fe or by the increasing heat of the flame. The precision of the method is good. A. O. JONES

354. Studies on tetralin derivatives. V. Reaction of hydroxyacetyl tetralin oximes with metal ions. Tsutomu Momose and Yoshito Masuda (Pharm. Inst., Med. Fac., Kyushu Univ., Katakatsu, Fuku-

oka). *Japan Analyst*, 1959, 8 (3), 153-157.—2-Acyl-5:6:7:8-tetrahydro-1-naphthoils (acetyl to α -decanyl) were prepared and converted into the oximes, the behaviour of which towards various metal ions was examined. Nickel forms a light-green ppt. in neutral soln., the limit of detection being 5 μg per ml. The max. absorption in CHCl_3 is at 380 $\text{m}\mu$. Copper forms a ppt. in neutral or acetic acid soln. (limit of detection, 5 μg per ml). The yellow chelate has max. absorption in CHCl_3 at 340 $\text{m}\mu$, the extinction being proportional to the concn. of Cu (<100 μg per ml). The length of the acyl chain has little effect on the limit of detection and the absorption characteristics.

K. SAITO

355. Use of tritium for the determination of hydrogen in metals. A. I. Chizhikov and V. K. Boyarshinov. *Metallurg. i Metalloved.*, 1958, 470-475; *Ref. Zhur. Khim.*, 1959, (8), Abstr. No. 27,071.—The method is based on an isotopic exchange between the H in the metal and a known amount of ^3H when the sample (12 to 50 g) is heated in a closed system, under conditions similar to those of the vacuum-fusion method (cf. Batalin, *Zavod Lab.*, 1953, 19, 544). The sample is introduced into a special apparatus (described) that has previously been de-gassed to a residual pressure of 1×10^{-4} torr. A known amount of ^3H is added to the system, which is then heated to the required temp. After equilibrium has been attained, the gaseous mixture is counted in a special counter, and the H content of the sample is calculated from the proportions of H and ^3H in the gaseous phase and the known amount of ^3H added to the system. The rate of attainment of equilibrium is controlled by means of gas samples of known specific activity. The determination occupies from 1.5 to 3 hr., and, with one exception, the results agreed well with those by conventional methods.

K. R. C.

356. Determination of lithium, sodium, potassium and calcium in Perhydrol by flame spectrography. W. Kemula, W. Brachaczek, D. Dancewicz and A. Hulanicki (Inorg. Chem. Dept., Warsaw Univ., Poland). *Chem. Anal., Warsaw*, 1958, 3 (5-6), 729-736.—The concn. of Li, Na, K and Ca in 30% H_2O_2 are determined by flame spectrography for the following approx. concn. (%): Li, 0.0006; Na, 0.02; K, 0.01; and Ca, 0.02. Ammonium dihydrogen phosphate is used as a spectral buffer. Mutual interference and the influence of other cations and anions are discussed. The coeff. of variation were—Li, $\pm 5.3\%$; Na, $\pm 3.0\%$; K, $\pm 3.4\%$; and Ca, $\pm 3.9\%$. H. DMOWSKA

357. Absorptiometric determination of traces of cadmium in Perhydrol and hydrofluoric acid. W. Kemula, W. Brachaczek and A. Hulanicki (Phys. Chem. Dept., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, 3 (5-6), 923-931.—After a preliminary decomposition of the sample, Cd is extracted from an alkaline soln. containing KCN and Na K tartrate by dithizone in CHCl_3 . The absorption due to cadmium dithizonate is then measured at 520 $\text{m}\mu$ in a 2-cm cell. The results are referred to a standard graph. The method is suitable for concn. from 1 to 8 μg , and the standard deviation is $\pm 0.2 \mu\text{g}$; Cu, Pb and Fe do not interfere in concn. $\gg 4000$ times that of Cd. H. DMOWSKA

358. Polarographic determination of lead and iron in Perhydrol, and copper, lead and iron in hydrofluoric acid and ammonium fluoride. W.

Kemula and S. Rubel (Dept. of Inorg. Chem., Warsaw Univ., Poland). *Chem. Anal., Warsaw*, 1958, 3 (5-6), 837-844.—Lead, Fe and Cu (0.0005 to 0.01%) are determined polarographically (after thermal decomposition of the sample) in a supporting electrolyte 0.01 M in triethanolamine and 0.1 M in KOH. Aluminium, Ca, Si and P do not interfere. The relative error in Perhydrol is 2.7% to 4.1%; in fluoro compounds 1.9 to 3.9%. H. DMOWSKA

359. New method of direct determination of argon and nitrogen. Tadashiro Koyama (Univ. Nagoya, Japan). *J. Earth Sci., Nagoya Univ.*, 1958, 6, 1-11 (in English).—Nitrogen is usually determined by removing O and CO_2 and measuring the change in vol. caused by its reaction with metallic calcium or barium. The direct determination of N by a quant. conversion of the nitride formed into NH_3 was studied, but the decomposition with water is too violent to give reproducible results. Good results can be obtained by the reaction of the nitride with glycerol. The apparatus and procedure are described. The method can be used for gases, water and soil, and is applicable in the presence of H and acetylene.

CHEM. ABSTR.

360. Determination of lithium in ammonium fluoride and in hydrofluoric acid. W. Kemula and A. Hulanicki (Inorg. Chem. Dept., Warsaw Univ., Poland). *Chem. Anal., Warsaw*, 1958, 3 (5-6), 721-728.—The concn. of lithium in fluorine compounds is determined by flame spectrography. Samples (≈ 10 g) are decomposed with HClO_4 , and Rb is added as the internal standard and K as a spectral buffer. The coeff. of variation is $\pm 5.7\%$ for the concn. range of 0.0004 to 0.0015%. H. DMOWSKA

361. Semi-quantitative spectrographic determination of lithium in ores and minerals. B. M. Maslennikov and L. V. Romanova. *Trudy Gos. Nauch.-Issled. Inst. Gorno-khim. Syr'ya*, 1958, (4), 230-232; *Ref. Zhur. Khim.*, 1959, (10), Abstr. No. 34,587.—The spectra are excited in an a.c. arc at 5 amp., with evaporation of the substance from a groove in the carbon electrode. The image of the end of the upper electrode is projected on to the edge of the diaphragm by a lens of 150 mm focal length. The spectra are photographed in the medium quartz spectrograph ISP-22 on Panchrome plates (of sensitivity 32 standard units), with exposure 60 sec., arc gap 2.5 mm and slit width 0.01 mm. The line 6707.8 \AA is used; the sensitivity of the determination is 1×10^{-4} %. In analysing carbonate rocks, standards are prepared in a base of CaCO_3 . The presence of $\geq 3\%$ of NaCl does not cause interference.

C. D. KOPKIN

362. Determination of lithium in spodumene ores. L. A. Shneider. *Obozashchenie Rud*, 1958, (3), 41-42; *Ref. Zhur. Khim.*, 1959, (9), Abstr. No. 30,971.—It is established that the usual methods of opening spodumene ores, by treatment with a mixture of HF and H_2SO_4 , ignition with oxalic acid, or fusion with alkali-metal sulphates, do not ensure the quant. extraction of Li (spectrographic analysis has shown that 1 to 1.5% of Li_2O remains in the undecomposed residue). An accurate method is described, based on the decomposition of the ore by ignition with a mixture of CaCO_3 and NH_4Cl (1:8). The residue is leached with water to dissolve alkali and alkaline-earth metals, and the latter are separated as carbonates; the filtrate is evaporated to remove ammonium salts, and the residue is

dissolved in water. The soln. is treated by the method of Rogers and Caley (*Ind. Eng. Chem., Anal. Ed.*, 1943, 15, 209). C. D. KOPKIN

363. Spectrographic determination of lithium hydroxide in potassium-lithium electrolytes. N. Ya. Ugnjachev and T. I. Tyutyunnikova. *Trudy Nauch.-Issled. Inst. Osnovoi Khim.*, 1958, 11, 307-309; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,284.—Dissolve the sample of electrolyte (10 g) in water, neutralise with dil. HCl and make up to 100 ml. Place 2 drops of the soln. on the flat end of a previously ignited carbon electrode, excite the spectra with an upper copper electrode in an a.c. arc at 6 amp., and photograph them in a medium spectrograph. The results are referred to a calibration curve of ΔS vs. $\log C$ with the lines Li 3232.6 and K 3446.7 Å. The error is $\pm 5\%$. C. D. KOPKIN

364. Analysis of lithium arsenide. E. H. Van Kooten, A. W. Mosen and G. R. Waterbury (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm., Rep. LA-1950, 1955*, 17 pp.—The sample is treated with water in a special apparatus, the arsine formed is absorbed in bromine water and the Li in the residual aq. soln. is determined by titration with standard acid. The entire sample is then re-combined, the excess of Br is boiled off and hydrazine hydrochloride and KBr are added. The As is distilled as AsCl, after the soln. has been made ≈ 6 N in HCl, and is determined by potentiometric titration with standard KBrO_3 soln. An average recovery of 100.1%, with a standard deviation of 0.1%, was obtained for 32 determinations of 17.86 mg of Li in the presence of 11 to 100 mg of arsenous oxide. An average recovery of 100.0%, with a standard deviation of 0.6%, was obtained for 21 determinations of 17 to 155 mg of As; the method is less reliable for smaller amounts of As.

NUCL. SCI. ABSTR.

365. Flame-photometric determination of sodium in calcium metal and calcium hydride. N. Ya. Ugnjachev, T. I. Tyutyunnikova and T. P. Dubrovina. *Trudy Nauch.-Issled. Inst. Osnovoi Khim.*, 1958, 11, 332-333; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,288.—When using a photometer with interference filters and an air-benzene vapour flame (cf. Kisilevskii and Tyutyunnikova, *Anal. Abstr.*, 1960, 7, 366), Ca interferes in the determination of Na and must be removed. The p.t.n. of Ca with ammonium oxalate leads to results for Na that are low by 25 to 50%. Good results are obtained by p.p.t. Ca with the equivalent amount of oxalic acid, with subsequent neutralisation with aq. NH_3 , and determining Na in the filtrate. The method enables 1% of Na to be determined with an error $\pm 4\%$. C. D. KOPKIN

366. Flame-photometric determination of sodium, potassium, lithium and calcium with the use of a liquid fuel. V. V. Kisilevskii and T. I. Tyutyunnikova. *Trudy Nauch.-Issled. Inst. Osnovoi Khim.*, 1958, 11, 318-325; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,289.—An apparatus is described in which an air-petrol vapour or air-benzene vapour flame can be used. The air is pumped into a carburettor, where it is saturated with the fuel vapour, and passes through guard tubes and two manostats; the burner is made of stainless steel and is cylindrical, with 69 holes each of 1.2 mm diam. Interference filters are used to isolate the resonance lines of Na, K and Li or the molecular

bands of CaO (615 m μ); selenium and silver sulphide photocells are used; the photocurrent is measured with a mirror galvanometer. Calibration curves are constructed from soln. with concn. of Na and K from 1 to 40 μg per ml, of Li from 18 to 1000 μg per ml, and of Ca from 65 to 3500 μg per ml. The determination of these elements in technical products is described. In determining Li in the presence of K (e.g., potassium-lithium electrolyte), the content of K in the soln. must first be determined, and a calibration curve constructed for Li from soln. containing the same amount of K.

C. D. KOPKIN

367. Colour-contrast reactions for the detection of potassium, ammonium, rubidium and thallium ions. T. Gaspar y Arnal (Univ., Valladolid, Spain). *Chim. Anal.*, 1959, 41 (4), 152-154.—In 50% aq. ethanol cobalt salts form a green ppt. with $\text{Ca}_2\text{Fe}(\text{CN})_6$, but do not react with $\text{CaK}_2\text{Fe}(\text{CN})_6$. For the detection of K^+ all ions up to and including those of group III and NH_4^+ are removed. To a soln. of the sample in aq. ethanol are added a neutral soln. of $\text{Na}_4\text{Fe}(\text{CN})_6$ and a calcium salt. If K^+ are present a white ppt. forms. A neutral soln. of a cobalt salt is added. If K^+ are present no further reaction occurs in the tube containing the sample, while a green ppt. appears in the reagent blank. If a molybdate is used in place of the cobalt salt and the soln. made slightly acid with acetic acid, a red colour appears in the absence of K^+ . The test is applicable with slight modifications to the detection of the other alkali-metal ions.

G. BURGER

368. Cationite paper. IV. Quantitative determination of total potassium-group and calcium-group metals in glass. H. Witkowski (Gen. Chem. Dept., Univ. Poznań, Poland). *Chem. Anal., Warsaw*, 1958, 3 (5-6), 1049-1052.—Finely ground glass (0.1 g) is evaporated to dryness with HF, then thrice with HCl and twice with acetic acid. The residue is dissolved in acetic acid and made up to 50 ml, and 0.5 ml is analysed chromatographically on paper containing the cationite L-W28 (H form) prepared by the method of Witkowski (cf. *Anal. Abstr.*, 1957, 4, 1386). Results for CaO plus MgO and Na_2O plus K_2O agree well with those by gravimetric and photometric procedures.

H. DMOWSKA

369. Determination of potassium, rubidium, caesium and ammonium by high-frequency titration with sodium tetraphenylboron. A. R. Vels and A. F. Ievin'sh. *Uch. Zap. Latv. Univ.*, 1958, 22, 95-99; *Ref. Zhur. Khim.*, 1959, (10), Abstr. No. 34,586.—Dilute an aliquot of the test soln., measured with a pipette or semi-micro burette, to about 25 ml in a 25- or 30-ml cell, and titrate from a semi-micro burette with 0.2 M Na tetraphenylboron (I) with a current frequency of 14 Mc/s, measuring the vol. of titrant to ± 0.005 ml. Find the end-point graphically from a curve of vol. of titrant (ml) vs. current (mA). The soln. of I is standardised against 0.1 N KCl. The results for K^+ , Rb^+ , Cs^+ and NH_4^+ in the absence of other salts are satisfactorily reproducible; with large amounts of other salts the accuracy decreases. In the presence of CaCl_2 and NaCl ($\text{K}^+/\text{Ca} = 1:2$; $\text{K}^+/\text{Na} = 1:5$), the total concn. of salts in the soln. should not exceed 0.02 N, while in the presence of MgSO_4 ($\text{K}^+/\text{Mg} = 1:5$), completely acceptable results are obtained with a total concn. of salts of ≈ 0.05 N. Substances that react with I (e.g., Ag^+ , Ti^{4+} , Cu^{2+} , Th^{4+} , Ce^{4+} , Hg^{2+} and organic

amines) interfere. The end-point is satisfactorily sharp both in weakly acid media ($\geq 0.01 N$ in HCl or H_2SO_4 , or $\approx 0.05 N$ in acetic acid) and in weakly alkaline media ($\geq 0.02 N$ in Na_2CO_3). The method is useful for the determination of K^+ in wood ash and molasses. C. D. KOPKIN

370. Separation of fission-product caesium by zirconium phosphate. T. V. Healy and B. L. Davies (A.E.R.E., Harwell, England). A.E.R.E. Report AERE-M 451, 1959, 6 pp.—Experiments are described in which Cs was adsorbed from 0.1 M HNO_3 on to zirconium phosphate resin to the extent of 0.6 mill-equiv. per g. The adsorption of Cs from more conc. acid was low, as was that of Ce from 0.1 M HNO_3 . The adsorption of Cs from fission-product concentrates at reduced acidities was very poor, and was attributed to constituents such as Fe and Al in the concentrates. G. J. HUNTER

371. Use of thiosemicarbazides in analysis. I. Detection and determination of copper with aryl and diaryl-thiosemicarbazides. N. V. Koshkin. *Trudy Leningr. Tekhnol. Inst. Pishch. Prom.*, 1958, **15**, 96-100; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,290.—It is shown that 1-phenyl- (I), 1:4-diphenyl- (II) and 1-phenyl-4-*o*-tolyl-thiosemicarbazide (III) form with Cu^{2+} intensely coloured water-soluble compounds which are extracted by isoamyl alcohol (IV). To detect Cu^{2+} , use a 1.5% soln. of I in acetic acid or a 0.1 to 0.05% soln. of II or III in acetone; in the presence of Cu a blue or green colour, respectively, is formed. The best results are obtained by shaking the test soln. with a 0.1% soln. of I, II or III in IV; after settling, the layer of IV is coloured blue (with I) or dark green (with II or III). To determine Cu^{2+} with I, to 45 ml of test soln. (sulphate or nitrate) add 5 ml of a 0.7% soln. of I in acetone and measure the extinction after mixing. When using II or III, to 30 or 35 ml of test soln. add 10 to 15 ml of acetone, make up to 50 ml with a 0.4 to 0.7% soln. of II or III in acetone, and measure the extinction. The sensitivity of the determination is increased by extracting the complexes with IV. To 50 or 70 ml of test soln. add 10 to 15 ml of a 0.05 to 0.1% soln. of I, II or III in IV, shake, and separate the layer of IV; repeat until all the Cu has been extracted, dilute the combined extracts to 25 or 50 ml with IV and measure the extinction. The method can be used to determine ≥ 0.7 mg of Cu^{2+} in 150 or 200 ml of soln. Most cations and anions do not interfere; in the presence of bismuth and antimony salts and other easily hydrolysable salts, carry out the determination in an HCl medium at pH 1, with subsequent extraction of the complexes with IV. In the presence of Hg_2^{2+} , Hg^{2+} and Ag^+ , the Cu^{2+} must be determined after considerable dilution. Chromium, Ni, Co and Fe do not interfere, but Sn^{2+} , MnO_4^- , CrO_4^{2-} and $Cr_2O_7^{2-}$ do. C. D. KOPKIN

372. Gravimetric determination of copper with tetraphenyloxalamidine. E. Papafil, M. Papafil, D. Furnica and M. Furnica (Univ. "Al. I. Cuza," Iasi). *An. Stiint. Univ. "Al. I. Cuza" din Iasi*, 1958, **4** (2), 139-142 (in French).—The method is based on the pptn. of a copper complex of the reagent in an aq. soln. of pH > 5 in the presence of NH_4Cl . *Procedure*—To a cold soln. containing between 0.006 g and 0.019 g of Cu is added 10 to 20 ml of 2 N NH_4Cl and water to 50 ml. Three to four times the theoretical amount of the reagent in 50 ml of hot ethanolic soln. (i.e., 0.04 to 0.012 g of

NN'N'''-tetraphenyloxalamidine) is added dropwise. A brown flocculent ppt. is formed immediately; the mixture is stirred vigorously for 5 to 10 min. and set aside for 15 min. The ppt. is filtered off, washed with cold water and calcined wet to eliminate the excess of reagent. The method is applicable in the presence of the alkali and alkaline-earth metals and heavy metals other than Fe, Cr, Al, Pb and Ag, which must first be separated. The max. errors are $+0.2\%$ and -0.11% . H. SHER

373. Analytical use of chelones. XVII. Murexide as indicator for macro- and micro-determination of copper with 1:2-diaminocyclohexanetetra-acetic acid. F. Bermejo Martinez and R. Rey Mendoza (Lab. for Anal. Chem., Univ. Santiago de Compostela, Spain). *Z. anal. Chem.*, 1959, **167** (4), 261-264.—The complex of Cu^{2+} with disodium 1:2-diaminocyclohexanetetra-acetate (I) is more stable than that with EDTA. With murexide as indicator, 0.064 to 96 mg of Cu is rapidly determined with an accuracy within $\pm 0.5\%$. Nickel, Co, Zn, Cd and Mn interfere. *Procedure*—Adjust the copper soln. with 2.5% aq. NH_3 to pH 9 to 10, dilute to 150 ml, add a little indicator (1 part of murexide to 100 parts of NaCl), and titrate with a soln. of I of appropriate molarity. The colour changes from yellow to reddish violet.

J. P. STERN

374. Differential spectrophotometric determination of copper in copper alloys. Kichinosuke Hirokawa (Res. Inst. of Iron, Steel and other Metals, Tohoku Univ., Katahira-cho, Sendai). *J. Japan Inst. Metals, Sendai*, 1958, **22** (4), 181-185.—The max. absorption of $CuCl_2$ in HCl shifts towards the violet with increase in the concn. of HCl, and is located at 950 $m\mu$ in 6 N HCl. The photometric determination of Cu (0.3 to 0.35 g) is carried out at this wavelength by the use of a reference soln. containing 0.3000 g of Cu per 100 ml of 6 N HCl. The temp. must be kept constant within 0.5°. The relative error is $< 0.3\%$ in the presence of $< 35\%$ of Sn, Zn and Al, $< 10\%$ of Cr, and $< 6\%$ of Pb. *Procedure*—Dissolve the sample (containing 0.3 to 0.35 g of Cu) in HCl (6 N) (10 ml) and H_2O_2 (30%) (5 ml) and heat until crystals of $CuCl_2$ appear. Dissolve the residue in 6 N HCl (100 ml) in a flask calibrated at 25° and measure the extinction in a thermostatically controlled cell. K. SAITO

375. New semi-micro method for the gravimetric determination of copper in the presence of mercury. V. Armeanu, N. Căpescu and G. Mihail (Polytech. Inst. Bucharest). *Bul. Inst. Polit. Bucureşti*, 1958, **20** (2), 89-92 (in French).—The method is based on the formation of a copper compound with *o*-phenylenediamine (I), and its pptn. in the form of a complex mercuric iodide. *Procedure*—To 50 ml of a neutral or slightly acid soln. containing 10 to 40 mg of a mixture of Cu and Hg (as chlorides or sulphates) is added a freshly prepared filtered 2% ethanolic soln. of I until the colour changes to blue-violet. The violet cryst. ppt. which begins to form is redissolved by dropwise addition of a soln. of H_2SO_4 (2 to 3%) until the colour changes to yellow-green. The complex is then pptd. by dropwise addition of a soln. of K_2HgI_4 containing a slight excess of KI, corresponding to the amount of Hg present in the test soln. (previously determined approximately). The pptn. is completed by shaking; the reddish-violet ppt. is allowed to settle for 10 to 15 min. and is filtered off on a sintered glass crucible. It is

washed 3 to 4 times with 3 to 4 ml of a freshly prepared soln. of I. (0.2%), 2 to 3 times with cold water, and then dried at 105°. The K_2HgI_4 soln. is prepared by the dropwise addition of 10% KI soln. to 5 to 10 ml of 1% $HgCl_2$ soln., shaking well until the ppt. of HgI_2 re-dissolves, followed by an excess of KI equivalent to the Hg present in the test soln. The probable error is $\pm 0.09\%$. Amounts of Cu between 10 and 40 mg in 50 ml of soln. can be determined in the presence of a similar concn. of Hg.

H. SHER

376. Determination of copper in steel, ferrous alloys, aluminium, chromium, cobalt, manganese and nickel. Extraction process with 2:2'-diquinolyl. A. J. Leeb and F. Hecht (Schoeller-Bleckmann Stahlwerke A.-G., Ternitz, Germany). *Z. anal. Chem.*, 1959, **168** (2), 101-106.—The procedure is based on the formation of a violet to purple complex by Cu^{+} with 2:2'-diquinolyl which is extracted by amyl alcohol. A simple method of dissolution involving the addition of formic acid avoids repeated evaporation, and details are given for many metals and alloys. The prepared soln. (25 ml) is boiled for 5 min. with 25 ml of water satd. with SO_4^{2-} , and 15 ml of $FeCl_3$ soln. (500 g in 1900 ml of water plus 100 ml of conc. HCl) is added to reduce all copper to Cu^{+} . The soln., or an aliquot of it after dilution to 100 ml (if the Cu concn. is $>0.02\%$), is treated with 2 to 3 ml of 50% aq. citric acid soln. and made alkaline (pH 5 to 6) by the dropwise addition of aq. NH_3 ; 2 ml of 5% aq. Na acetate soln. is added, and the volume is made up to 40 ml with water in a separating-funnel. Extraction is then carried out for 2 min. with 10 ml of 2:2'-diquinolyl soln. (0.05% in amyl alcohol). The extinction of the extract is measured in a photometer and the Cu content determined by reference to a calibration curve. The method is applicable to Cu contents from 0.001 to 2%. The soln. to be extracted should contain a maximum of 110 μg and a minimum of 6 μg of Cu. A large excess of Ni, Cr or Co does not interfere.

S. M. MARSH

377. Determination of copper in fused mixtures of sodium, zirconium and uranium fluorides. U.K.A.E.R.E. (Res. Group, Woolwich Outstation, C.37, Royal Arsenal, Woolwich, London, S.E.18). AERE-AM 41, 1959, 5 pp.—The method is based on that of Riley and Sinhaseni (*Analyst*, 1958, **83**, 299) and is written with full details by E. Booth and A. Parker.

378. Three different methods of determining copper in chalcopyrite concentrates. J. Herrero Maisterra. *Chim. Anal.*, 1959, **41** (5), 186-188.—Rapid electrolytic, absorbiometric and volumetric (titration with $Ni_2S_2O_8$ soln.) procedures are given for determining Cu in the soln. obtained after roasting the sample (1 g) at 600° to 700° (15 min.), treating the residue with warm conc. HNO_3 , diluting with H_2O , boiling and filtering. Each method has a coeff. of variation of $\approx 0.4\%$ (10 to 12 analyses).

W. J. BAKER

379. Alternating-current polarography of copper and zinc in a supporting electrolyte containing ammonium chloride and ammonia. Kamihiko Itsuki and Fukunosuke Suzuki (Osaka Refinery, Mitsubishi Metal and Mining Co., Shinkawasaki-cho, Kita-ku). *Japan Analyst*, 1959, **8** (2), 89-91.—The characteristics of a self-balancing a.c. polarograph were examined with Cu and Zn in a supporting electrolyte M with respect to NH_4Cl and aq. NH_3 .

The effect of temp. (15° to 30°) is less marked than with d.c. polarography. A small difference in the distance between the electrodes (5 to 20 mm) does not affect the results. The wave height decreases with increase in concn. of gelatin and with increase in the applied a.c. voltage, which must be kept constant so as to keep the concn. vs. wave-height plot linear. The peak height is also affected by dissolved oxygen, but neither the reproducibility nor the linearity of the working curve is affected. The use of gelatin needs care, as its effect on the peak height is large.

K. SAITO

380. Paper-chromatographic separation of copper, silver and gold. G. Weidmann and J. Drabner (Inst. f. anorg. u. anal. Chem., Univ. Graz, Austria). *Öst. Chem.Ztg.*, 1959, **60** (5), 128-139.—A good separation of Cu^{2+} , Ag^{+} and Au^{3+} is possible with tri-n-butyl phosphate as solvent. Before use, the solvent is equilibrated with HCl of varied concn. and is mixed with methanol in the ratio 2:1. Gold moves with the solvent front, whilst Ag remains near the origin. The R_F value for Cu increases with increase in the concn. of the HCl used for equilibration up to 9.5 N, when a constant value of 0.57 is obtained.

J. H. WATON

381. Determination of silver with radioactive silver dithizonate by the isotopic exchange method. Nobuo Suzuki (Chem. Dept., Fac. of Sci., Tohoku Univ., Katahira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (4), 373-375.—The isotopic exchange between Ag^{+} ($<5 \mu g$) in 0.5 N H_2SO_4 and Ag dithizonate in CCl_4 is completed by shaking for 1 min.; a determination of Ag ($<0.1 \mu g$) can thus be carried out. The exchange is also rapid in 0.1 N HNO_3 , N acetic acid or an acetate buffer of pH 5. In the presence of Cu, the rate of exchange decreases, but this effect is masked with EDTA. In the presence of $>0.1 M$ KNO_3 , $NaNO_3$ or $Ca(NO_3)_2$, the exchange equilibrium cannot be reached. The formula given previously (*cf. Anal. Abstr.*, 1960, **7**, 633) is used.

K. SAITO

382. Neutron activation analysis of silver by the use of a radium-beryllium source. Yuzuru Kusaka (Fac. of Sci., Konan Univ., Higashinada-ku, Kobe). *Japan Analyst*, 1959, **8** (2), 111-115.—With the aid of a new device (illustrated), which permits the rapid measurement of the activity due to ^{110}Ag (half-life, 24 sec.), a neutron activation analysis was effected with a Ra-Be source (Ra, 50 mg). The sample (e.g., a mixture of Ag_2O and CuO) is placed beneath the mica window of a Geiger counter, and the Ra-Be source is inserted beneath the sample, the whole being embedded in paraffin wax. After irradiation for a few minutes, the source is removed and the activity measured. To improve the accuracy, the procedure of repeated short-time irradiation and measurement was adopted.

K. SAITO

383. Elution of precious metals from anionites after adsorption. A. B. Davankov and V. M. Laufer. *Zhur. Prikl. Khim.*, 1959, **32** (4), 727-734.—It is shown that acid soln. of thiourea, or organic solvents such as acetone, ethanol and ethyl acetate to which 5% of HCl (sp. gr. 1.19) and 5% of H_2O have been added, recover Au practically completely from ion-exchange resins after adsorption in the form of the complex anions, $Au(CN)_4^{2-}$ and $AuCl_4^{2-}$; this is true not only with pure soln., but also with highly impure industrial soln. of $KAu(CN)_4$ or $NaAu(CN)_4$ (with these impure soln., elution of gold ions with NaOH soln. is not always satisfactory). The

$\text{Au}(\text{CN})_2^-$ adsorbed from pure soln. are very stable to the action of reducing agents and are completely recoverable from resins by aq. soln. of strong or weak bases, but AuCl_4^- adsorbed by anionites are easily reduced to the metal; by alternating the processes of adsorption and reduction, pure gold may be accumulated on the anionite. K. R. C.

384. Determination of free metal and carbide carbon in beryllium metal. U.K.A.E.A. (Res. Group, Chem. Div., Chatham Outstation, Kent). AERE-AM 44, 1959, 4 pp.—The method is based on standard analytical practice and is described in detail by J. Walkden. (Note—One of the formulae has subsequently been amended.) G. S. ROBERTS

385. Determination of combined nitrogen in beryllium metal. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 43, 1959, 4 pp.—The method is based on standard analytical practice and is written with full details by J. Walkden.

386. Determination of combined oxygen in beryllium metal. C. G. Wallace [U.K.A.E.A. (Res. Group), Chem. Div., Woolwich Outstation, Royal Arsenal, London]. AERE-AM 16, 1959, 7 pp.—Beryllium oxide (0.01 to 5%) is determined by reaction of the metal with acidic $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ soln. at pH 4; the residual BeO is extracted with NH_4F and the $(\text{BeF}_4)^{2-}$ are converted into $\text{Be}(\text{OH})_4^-$. This is determined by reaction with NaF and titration of the liberated alkali. The coeff. of variation in the range 0.1 to 2% is stated to be about 15% for powders and 5 to 10% for other forms of the metal. (Cf. A.E.R.E. Report C/R 2509.) J. P. STERN

387. Rapid routine method for the determination of sub-microgram and microgram amounts of beryllium in filter-paper. T. M. Florence (Atomic Energy Comm. Res. Estab., Lucas Heights, N.S.W., Australia). *Anal. Chim. Acta*, 1959, 20 (5), 472-476.—Concn. of Be as low as 0.05 μg in filter-paper smears can be determined fluorimetrically with morin (0.025%, w/v, in ethanol) after the removal of interfering ions (Cu, Zn, Fe, U) by adsorption, from 9 N HCl, on a column (11 cm \times 0.6 cm) of De-Acidite FF and the addition to the eluate of EDTA (disodium salt) to complex Ca and Ni. Max. fluorescence is attained at a morin concn. of 5×10^{-4} % in 0.05 N NaOH. The extinction of the blank (filter-paper plus acids used for digestion) is usually < 0.03 μg of Be. Thorium and Cr interfere seriously as neither is retained on the resin column; the max. permissible concn. for an error < 5% are 80 times that of Be for Th and 100 times that of Be for Cr. Twenty filter-paper smears can be analysed in < 6 hr., with $\approx 100\%$ recovery of Be. W. J. BAKER

388. Solvent extraction of beryllium as acetylacetone. Tsunenobu Shigematsu and Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Sakyoku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, 80 (2), 159-162.—The extraction of Be acetylacetone with CHCl_3 (Steinbach and Freiser, *Anal. Chem.*, 1953, 25, 881) was examined with reference to its use in the separation of Be from fission products. On the micro scale, the colorimetric determination of Be with Eriochrome cyanine R (C.I. Mordant Blue 3) (cf. Hill, *Anal. Abstr.*, 1958, 5, 2900) was employed. Approx. 97% of the Be is extracted from fission products with CHCl_3 (10, 5, 5 ml)

from an aq. soln. (50 ml) of pH 7 to 8 in the presence of carrier Be (10 μg), EDTA soln. (10%, 2 ml), acetylacetone soln. (5% aq., 1 ml) and NaCl (2.5 g). K. SAITO

389. Spectrophotometric determination of beryllium with acetylacetone and its application to the analysis of aluminium alloys. Tsunenobu Shigematsu and Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Sakyoku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, 80 (2), 162-165.—The photometric determination of Be at 295 μm with acetylacetone (I) (cf. Adam *et al.*, *Brit. Abstr. C*, 1952, 372) was examined with reference to the removal of the excess of I in the alkaline form (max. absorption, 245 μm) from the CHCl_3 layer, and was applied to aluminium alloys containing < 0.01% of Be. By washing the organic layer (20 ml), separated from an aq. soln. of pH 6 to 9, with 0.1 N NaOH (3 \times 50 ml), most of the I is removed, the Be remaining in the CHCl_3 layer. In the presence of > 0.5 g of Al, the extraction must be repeated. *Procedure*—Dissolve the sample (0.5 g) in conc. HCl (5 ml) and dilute to 100 ml. To a 5 to 10-ml aliquot add EDTA soln. (10%, 20 ml) and NaCl (2.5 g), and adjust the pH to 7. Add I soln. (5%, 5 ml), restore the pH to 7 and shake with CHCl_3 (10, 5, 5 ml). Evaporate the CHCl_3 to dryness, heat to white fumes with HClO_4 (1 ml) and add water, EDTA soln. (10%, 15 ml) and NaCl (2.5 g); bring the pH to 7, add I soln. (5%, 1.5 ml) and extract with CHCl_3 (20 ml). Wash the organic layer with 0.1 N NaOH (3 \times 50 ml), dry it with anhyd. Na_2SO_4 and measure the extinction at 295 μm . K. SAITO

390. Separation of beryllium from polyvalent cations with a dialyl phosphate complexing resin. J. Kennedy and V. J. Wheeler (A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1959, 20 (5), 412-415.—Beryllium can be separated quant. from Ca, Sr, Cu, Zn, Al, Fe^{III}, Cd, Hg^{II}, Bi, Po^{IV} and lanthanides by adsorption on to a short column of sodium dialyl phosphate polymer (cf. Kennedy *et al.*, *J. Appl. Chem.*, 1958, 8, 461) in the presence of EDTA (disodium salt) (2.5%, w/v); no adsorption of the other cations takes place. The Be can be eluted with 0.5 M NH₄F or 2 N HNO₃. There is quant. adsorption of UO_2^{2+} also, but these can be quant. eluted with Na_2CO_3 leaving Be on the column. The saturation capacity of the polymer for Be is very high compared with that of sulphonated resins. W. J. BAKER

391. Determination of beryllium oxide in beryllium fluoride. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 47, 1959, 2 pp.—The method is based on standard analytical practice and is described in detail by J. Walkden.

392. Determination of iron in beryllium compounds (fluoride, hydroxide and ammonium fluoroberyllate). U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 49, 1959, 4 pp.—The method is based on standard analytical practice and is described in detail by J. Walkden.

393. Determination of copper in beryllium compounds (fluoride, hydroxide and ammonium fluoroberyllate). U.K.A.E.A. (Res. Group, Chem. Div., H.M. Gun Wharf, Chatham, Kent). AERE-AM 53, 1959, 3 pp.—The method is based on standard analytical practice and is written with full details by J. Walkden.

394. Spectrophotometric determination of a trace amount of magnesium in pure sodium chloride with xylidyl blue. Kiyoshi Sato and Keiichi Takeuchi (Osaka Ind. Res. Inst., Oyodo-ku, Osaka). *Japan Analyst*, 1959, **8** (3), 190-196.—The method of Mann and Yee in which xylidyl blue [3-hydroxy-4-(2-hydroxy-5-sodiumsulphophenylazo)-2-naphtho-2':4'-xylidide] (I) is used for the photometric determination of Mg (cf. *Anal. Abstr.*, 1956, **3**, 2009; 1957, **4**, 2109) is applied to the analysis of pure NaCl to be used as a primary standard. Sodium chloride (<1 g) increases the extinction of Mg at a concn. <2 μ g per ml and decreases it at >2 μ g. Nevertheless a linear relationship between the extinction and the concn. of Mg (<8 μ g per 25 ml) holds for a given amount of NaCl. The determination of \approx 0.0002% of Mg is carried out by the "linear extinction method." The sample soln. (1 g of NaCl per 10 ml) (i) with and (ii) without added Mg soln. (10 p.p.m., 0.4 ml) and (iii) containing the same amount of added Mg plus EDTA soln. (0.001 M, 0.5 ml, as a masking agent for Mg towards I), are mixed with I soln. (0.015% in ethanol, 2.5 ml), borax soln. (0.04 M, 1 ml) and ethanol (10 ml) and made up to 15 ml with water; the extinctions are measured at 510 μ m after 30 min., the blank values for water and for the reagents being measured without the NaCl in the same way. The three extinctions lie on a straight line, the difference between (i) and (ii) corresponding to the amount of added Mg, and that between (ii) and (iii) to the Mg in the sample. K. SAITO

395. Micro-determination of calcium. A. B. Gilbert (Dept. of Zoology, King's College, Univ. of Durham, Newcastle upon Tyne). *Nature*, 1959, **183**, 1754-1755.—Eriochrome black T (C.I. Mordant Black 11) is superior to Calcon (C.I. Mordant Black 17) (cf. Hildebrand and Reilley, *Anal. Abstr.*, 1957, **4**, 2518) as indicator in the micro-determination of Ca^{++} at pH 12 to 13, because it can be used in high concn. without affecting the accuracy of the results. A. R. ROGERS

396. Chelatometric titration of calcium using a mixed indicator. J. S. Bullock and R. H. Maier (Dept. of Agric. Chem., Univ., Tucson, Ariz., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (5), 419-422.—For the complexometric determination of microgram amounts of Ca in the presence of relatively high concn. of other ions (as in soils and clays), a mixed indicator can be used provided that KCN (200 mg) is present to obviate the interference of other metals (except Mn and Sr). If Eriochrome blue SE (C.I. Mordant Blue 13) plus Naphthol green B (C.I. Acid Green 1) (0.1% methanolic soln. of each) is used, the addition of methanol (15 ml) improves the visibility of the end-point, except in titrations of macro amounts of Ca. W. J. BAKER

397. Determination of calcium and strontium (calculation method). A. S. Ruchik and L. S. Starostina. *Trudy Gos. Nauch.-Issled. Inst. Gorno-Khim. Sýr'ya*, 1958, (4), 242-246; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,299.—The method described for the determination of Ca and Sr (without their separation) is based on pptn. as oxalates and ignition to oxides. *Procedure*—Fuse the sample with Na_2CO_3 and dissolve the melt in 10% HCl. Precipitate the tervalent metals as hydroxides from two aliquots of the soln., and add to the filtrates 10 ml of 10% acetic acid and 25 to 30 ml of 0.2 N oxalic acid. Dilute to between 70 and 80 ml, and precipitate Ca and Sr oxalates with

aq. NH_3 , adding 40 or 50 ml of ethanol to ensure complete pptn. of Sr oxalate. After 12 hr. filter off the ppt. and wash them with 50% ethanol. Ignite one ppt. to CaO and SrO at 1000°; dry the second ppt. at 60° to 70° to remove ethanol, add 60 to 70 ml of water and 15 to 20 ml of 10% H_2SO_4 , heat to 80° and titrate the oxalate with 0.1 N KMnO_4 . If the wt. of CaO is c , the wt. of SrO is s , the wt. of CaO plus SrO is p and the amount of 0.1 N oxalic acid used in the pptn. of the oxalates is A_1 , then $c = 0.00611 A_1 - 1.1794 p$, and $s = p - c$. The value of A_1 may also be determined by pptn. with Ca^{++} of the excess of oxalic acid in the filtrate, and volumetric or gravimetric determination of the oxalate. With a sample containing little Sr or Ca, add known amounts of these elements. The method may be used for the analysis of limestone and gypsum. C. D. KOPKIN

398. Use of EDTA in the separation of barium, strontium and calcium. L. I. Afanas'eva (Lab. of Pre-Cambrian Geology, Acad. Sci., Leningrad). *Zhur. Anal. Khim.*, 1959, **14** (3), 294-297.—Radioactive indicators were used to study the separation of Ba, Sr and Ca as sulphates in the presence of EDTA. The results of Balczo and Doppler (*Z. anal. Chem.*, 1956, **152**, 321) showing that Ba can be quant. separated from Sr by pptn. of BaSO_4 from an EDTA soln. (pH \approx 8) are confirmed but, contrary to these authors' views, it is shown that Sr can be quant. pptd. as sulphate from an EDTA soln. It is suggested that Sr and Ca be separated by pptg. SrSO_4 from an EDTA soln. at pH \approx 5; the amount of co-pptd. Ca is \geq 1.2% of that present. K. R. C.

399. Quantitative paper chromatography and direct titrimetric finish for determination of zinc spot concentrations. A. Lacourt and P. Heyndryckx (Microchem. Dept., Univ., Brussels, Belgium). *Microchem. J.*, 1959, **3** (2), 181-189.—A titrimetric finish is described for the determination of minute amounts of elements chromatographed on paper according to a standardised procedure, with the object of eliminating the intermediate stage of elution. Titration of the spots with EDTA was successful for amounts of Zn > 4 μ g, and was also used to determine Zn after separation from Co and Cu. D. F. PHILLIPS

400. Analytical applications of thermogravimetry. V. Thermogravimetric analysis of lithopone. F. Burriel-Martí, C. García Goyanes and Q. Alvarez (Dept. Quím. Anal. C.S.I.C., Madrid). *Afínidad*, 1959, **36**, 51-55.—An industrial method for the rapid and reasonably accurate analysis of lithopone is described, and compared with previous methods. The thermal behaviour of ZnS and ZnSO_4 is also studied; a stable anhydrous ZnSO_4 occurs at 285° to 700°, which is transformed quant. into ZnO at 900°. C. A. FINCH

401. Quantitative absorption analysis of cadmium sulphate. N. P. Grudinskina. *Trudy Vses. Nauch.-Issled. Inst. Metrol.*, 1958, [34 (94)], 58-60; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,354.—The absorption spectra of soln. of ZnSO_4 , $\text{Pb}(\text{NO}_3)_2$ and CuSO_4 are studied and a method is developed for determining admixtures of Cu, Pb and Zn in soln. of CdSO_4 . *Procedure*—Place the soln. in a 100-mm quartz cell; photograph the spectra on spectrograph Q-24 on diapositive plates with a hydrogen lamp as the light source. Determine the amounts of the impurities by comparison of the absorption spectra.

of the samples with the spectra of soln. of CdSO_4 containing known amounts of Zn, Pb and Cu. The error is $\geq 40\%$.

C. D. KOPKIN

402. Quantitative determination of mercury(I) and mercury(II) with 1-phenylthiosemicarbazide. N. V. Koskin. *Trudy Leningr. Tekhnol. Inst. Pishch. Prom.*, 1958, 15, 91-95; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,302.—It is shown that 1-phenylthiosemicarbazide (I) forms with Hg^{2+} an extremely stable water-soluble coloured complex of the composition $[\text{Hg}(\text{C}_6\text{H}_4\text{NHNCNSNH}_2)_2]^{2+}$, which is suitable for the volumetric determination of Hg^{2+} and Hg^{2+} in the presence of CuNO_3 as indicator. In the determination of Hg^{2+} , metallic mercury is formed ($\text{Hg}_2^{2+} \rightleftharpoons \text{Hg}^{2+} + \text{Hg}$) and, to remove its influence, the soln. of I (in 70 to 80% acetic acid) is diluted before the determination (75 to 100 ml of water to 1 ml of an approx. 0.5 N soln. of I in acetic acid). To determine Hg^{2+} , add 1 or 2 drops of 0.1 N CuNO_3 to a soln. of I and titrate with the test soln. until the blue colour of the soln. changes to yellow; to determine Hg^{2+} , add 0.5 to 1 ml of 0.1 N CuNO_3 to a dilute soln. of I and titrate with the test soln. until the blue colour changes to grey-yellow. To determine Hg^{2+} or Hg^{2+} in the presence of Cl^- and Br^- , add an excess of NaOH to the test soln., filter off and wash the ppt., dissolve it in HNO_3 and determine Hg as described above. Most cations and anions do not interfere, but Ag^+ , Cl^- , Br^- and Sn^{2+} do. The titration may be carried out in acid medium over a wide pH range.

C. D. KOPKIN

403. Cerimetric determination of mercury(I). G. Jagga Rao and K. Bhaskara Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, 168 (2), 81-83 (in English).—Univalent Hg may be titrated directly with $\text{Ce}(\text{SO}_4)_2$ in 4 N HCl in the presence of ICl (I); CCl_4 is used as an extractive indicator since I interferes with internal redox indicators. A soln. of I (0.02 M, 5 ml) is added to an aliquot of the mercurous salt soln., and conc. HCl and water are added to give a soln. 4 N in acid and a total volume of 50 ml. After cooling, 5 ml of CCl_4 is added and the soln. is titrated with $\text{Ce}(\text{SO}_4)_2$ soln. The end-point is reached when the soln. becomes clear and the purple colour of the CCl_4 is discharged. Sulphate ions do not interfere in concn. $\geq 1.0\text{ N}$. The advantages of the method are that it is direct and can be carried out at room temp., and no correction factors are necessary. S. M. MARSH

404. Determination of bivalent mercury in the presence of chloride, bromide and heavy metals. E. Jackwerth and H. Specker (Inst. for Spectroscopy, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1959, 187 (4), 269-271.—The partition coeff. of HgI_2 between H_2O and cyclohexanone (I) is high. Thus Hg^{2+} can be separated from other elements by adding I- and extracting; other metals react only after complete conversion of the Hg into HgI_2 and/or $(\text{HgI})_2^-$. The next element to react is Bi, and the red BiI_3 is a useful indicator for the titration of Hg with standard I- in the presence of I (and with continuous stirring). Thus 10 mg of Hg can be determined with an accuracy within $\pm 1\%$. Most common cations, and Cl^- and Br^- do not interfere; Tl, Ag and SCN^- interfere. In the presence of coloured ions, the colour of the organic phase only is observed, otherwise the colour of the stirred suspension.

J. P. STERN

405. Rapid, accurate semi-micro method for the gravimetric determination of mercury in the presence of copper. V. Armeanu, N. Caplescu and G. Mihail (Polytech. Inst., Bucharest). *Bul. Inst. Polit. Bucaresti*, 1958, 20 (2), 93-96 (in French).—

The method is based on the quant. ptn. of the Cu as CuI , filtration of the soluble K_2HgI_4 , and ptn. of the Hg as a complex with copper-o-phenylenediamine (I). *Procedure*—To 50 to 100 ml of the neutral test soln. is added dropwise 10% KI soln. until the red ppt. re-dissolves and the colour changes to yellow. The ppt. of CuI is filtered off and washed 2 or 3 times with water. The free iodine in the filtrate is eliminated by the dropwise addition of 10% $\text{Na}_2\text{S}_2\text{O}_3$ soln. until the filtrate is decoloured, and the soln. is treated with I with continual shaking until ptn. is complete. The reddish-violet ppt. is filtered off, and washed several times with 3 to 4 ml of the diluted reagent (1:10), then 3 to 4 times with 3 to 4 ml of water, and dried at 105°. I is prepared by adding a 2% ethanolic soln. of o-phenylenediamine to 5 to 10 ml of 2% CuSO_4 soln. until the colour ceases to change. The soln. is then acidified with 3% H_2SO_4 until the ppt. first formed is re-dissolved and the colour changes to yellow. The probable error is $\pm 0.08\%$.

H. SHER

406. Fluorimetric determination of boron with resacetophenone as a reagent. G. Gopala Rao and N. Appalaraju (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, 167 (5), 325-329 (in English).—In conc. H_2SO_4 soln. resacetophenone (I) gives a blue fluorescence with H_3BO_3 when irradiated at 3650 Å. Boric acid (1%) (0.2 ml) is added to 10 ml of reagent soln. (0.5% of I in H_2SO_4) and diluted to 25 ml with H_2SO_4 . The fluorescence obtained reaches its maximum immediately and remains unchanged for 6 months. The intensity of the fluorescence is proportional to H_3BO_3 concn. up to 7 mg of H_3BO_3 , but with > 8 mg it decreases with increasing H_3BO_3 content.

T. R. ANDREW

407. Spectrophotometric determination of boron in reactor materials. II. Determination in ammonium fluoride. T. Nowicka-Jankowska and H. Szyszko (Polish Acad. Sci., Warsaw). *Chem. Anal. Warsaw*, 1958, 3 (5-6), 969-976.—The method previously described (cf. *Anal. Abstr.*, 1957, 4, 3592) for the determination of 0.5 to 10 μg of B with carmine has been modified for application to ammonium fluoride. The interference of F^- has been eliminated by adding $\text{Al}_2(\text{SO}_4)_3$ during the distillation and to the distillate; 0.5 to 5 p.p.m. of B can be determined in ammonium fluoride with a coeff. of variation of $\pm 20\%$.

H. DMOWSKA

408. Complexometric titration of aluminium and iron in a binary mixture. Takeo Danzuka and Keihei Ueno (Dojin Yakukagaku Kenkyusho, Izumi-cho, Kumamoto). *Japan Analyst*, 1959, 8 (2), 126-128.—The use of Variamine blue B (C.I. Azoic Diazo Component 36) as an indicator for the EDTA titration of Fe^{2+} at pH 2.2 to 2.5 (Erdey and Rády, *Anal. Abstr.*, 1956, 3, 2484; Flaschka, *Anal. Abstr.*, 1954, 1, 2416) is satisfactory in the presence of Al. The error increases with increase in the molar ratio of Al to Fe (e.g., $\pm 1\%$ for a ratio of Al to Fe of 1, $\pm 3\%$ for a ratio of 4, and $\pm 5\%$ for a ratio of 9); presumably because a part of the Al is titrated together with the Fe. The sum of Al and Fe is titrated with EDTA at pH 3 to 4, with Cu-1-(2-pyridylazo)-2-naphthol as indicator.

K. SAITO

409. Analysis of aluminium and aluminium-base alloys using d.c. arc. J. Haaland (Joint Estab. for Nuclear Energy Res., Kjellar, Norway). *Spectrochim. Acta*, 1959, (3-4), 270-280.—The sample is ground to powder and passed through a 50-mesh sieve. Weighed portions of 3 mg are loaded into an undercut graphite cup-electrode and arced to completion, the spectra being photographed and evaluated with a comparator-densitometer. The accuracy of the mean of 3 determinations is $\pm 10\%$ (relative).

P. T. BEALE

410. Photometric determination of aluminium in phosphate furnace slags. B. B. Evzina. *Sooobshch. Nauch.-Issled. Rabot i Novoi Tekh. Nauch. Inst. po Udobr. i Insektifungitsidam*, 1958, (8), 87-90; *Ref. Zhur., Khim.*, 1959, (10), Abstr. No. 34,601.—In the method evolved, preliminary removal of Fe is unnecessary. To 0.1 g of slag add water (2 ml), HCl (sp. gr. 1.19) (3 ml), HNO₃ (sp. gr. 1.40) (2 ml) and 10% H₂SO₄ (4 ml), boil for 5 min. and evaporate to dryness. Dissolve the residue in *N* HCl (5 ml) and water (15 ml), make up to 250 ml and filter. Dilute 5 ml of the filtrate to 40 ml, add 5% ascorbic acid soln. (0.2 ml), 25% Na acetate soln. (0.2 ml) and 0.05% stilbazo soln. (2 ml), make up to 100 ml with acetate buffer soln. (pH 5.4) and after 10 min. measure the extinction in 30-mm cells, with a green filter. The determination takes ≈ 1 hr. The results agree well with those of the gravimetric method.

C. D. KOPKIN

411. Rapid colorimetric determination of aluminium in raw materials and fluxes used in lead production. L. N. Krasil'nikov and L. I. Maksal. *Sb. Nauch. Trud. Vses. Nauch.-Issled. Gorno-Metallurg. Inst. Tsvet. Met.*, 1958, (3), 253-257; *Ref. Zhur., Khim.*, 1959, (10), Abstr. No. 34,598.—It is shown that the procedure with stilbazo proposed for the photometric determination of Al in slags and agglomerates (*cf. Anal. Abstr.*, 1958, **5**, 4024) is a suitable one. For products with a low content of Al (<1%) it is recommended that the sample be increased to 0.3 g; the aliquot of the soln. taken for the photometry may also be increased to 10 ml, so that it contains 20 to 30 μ g of Al. To widen the concn. limits in which Beer's law is obeyed, the amount of stilbazo used should be increased: for 50 ml of soln. use 5 ml of a 0.06% soln. In addition to the previously reported interference of Pb, Zn, Si, Ca, Cu and Fe, the influence of As, Sb and Mn is studied, and it is shown that these do not interfere, even in amounts considerably greater than their possible content in the raw material and fluxes (up to 10% of As and Sb, and 3% of Mn). To eliminate losses of Al by adsorption on the Fe(OH)₃ ppt. (which increase with increase in concn. of Fe and depend on the duration of fusion of the sample, owing to attack on the iron crucible), constant conditions must be observed during the fusion of sample and standard. The relative error of the determination as compared with the gravimetric phosphate method is $> 10\%$; the determination takes 40 to 60 min. The method may be used for process control.

C. D. KOPKIN

412. Micro-detection of gallium with alizarin red S in the presence of anion-exchange resin. Kiyoshi Kato and Hidetake Kakihana (Municipal Tech. High Sch., Kitae-cho, Nakamura-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (3), 282-284.—The limit of detection for Ga with alizarin red S (C.I. Mordant Red 3) (I) is reduced to 0.03 μ g (limiting dilution 1 in 1×10^{-6}) by the use of a particle of Dowex 1-X1 (acetate form,

50 to 100 mesh) on a spot plate at pH 5 to 7. A similar limit of detection was obtained by the use of the resin impregnated with I. The sample is mixed with a saturated NH₄Cl soln. and 0.3 *N* aq. NH₃ (one drop each) and one particle of the resin is added. The colour changes from violet to red after 6 hr. Interfering ions are Al, In, Mo, W, Zr, Sn, V, Th, Bi, Cr, Fe, U, Ti and Si. K. SAITO

413. Quantitative analysis of indium. I. Volumetric determination by the use of 8-hydroxyquinoline. Teiichi Matsumae (Gov. Ind. Res. Inst., Hirate-machi, Kitaku, Nagoya). *Japan Analyst*, 1959, **8** (2), 97-99.—Indium (<50 mg) is pptd. with 8-hydroxyquinoline in an acetate buffer of pH 4.4 and dissolved in 1.5 *N* HCl (60 ml). The soln. is slightly over-titrated with KBrO₃ soln. (2.79 g in 1 litre of 2.4% KBr soln. containing 0.2% of NaOH) to methyl red, and the excess of titrant is titrated with 0.1 *N* Na₂S₂O₈ in the presence of KI (2 g). There is no interference from Pb, Mn and Cd, or from Sb in the presence of tartrate; Fe, Zn and Cu must be previously removed.

II. Gravimetric and volumetric determination of indium with 8-hydroxyquinaldine. Teiichi Matsumae. *Ibid.*, 1959, **8** (2), 99-102.—8-Hydroxyquinaldine (I) (2% in 4% acetic acid) precipitates In (2 to 20 mg) in an acetate buffer or a tartrate buffer of pH 6 to 9, and the ppt. is dried at 110° to constant wt. Alternatively, the ppt. is dissolved in dil. HCl and titrated with KBrO₃ soln. as described above. Metals forming ppt. with I under the conditions given (Bi, Cd, Cr, Co, Cu, Fe, Mg and Mn) interfere.

III. Spectrophotometric determination of indium with arsenazo. Teiichi Matsumae. *Ibid.*, 1959, **8** (3), 167-170.—In an acetate buffer of pH 5.6 to 6.3, arsenazo (0.1% aq. soln., 1 to 3 ml) gives a violet chelate (max. absorption, 580 μ m) with In; Beer's law is obeyed up to 250 μ g of In per 25 ml. Tartrate and PO₄³⁻ diminish the coloration. Indium is extracted with diisopropyl ether from 7 M HBr, the org. layer is evaporated with HNO₃ and the residue submitted to photometry. The interference of Zn (<100-fold), Cu (<40-fold) and Pb (<20-fold) is thus eliminated. There is no interference from Fe^{II}; Fe^{III} is reduced with ascorbic acid. This method is applicable to the analysis of zinc blende and intermediates for the electrolytic refining of zinc.

K. SAITO

414. Determination of indium by the radio-activation method. G. Irving. *Trudy Komiss. Anal. Khim. Akad. Nauk SSSR*, 1958, **9** (12), 249-263; *Ref. Zhur., Khim.*, 1959, (10), Abstr. No. 34,602.—It is shown that In may be determined by the activity of ¹¹⁴In, obtained from ¹¹³In (which constitutes 95.77% of the natural element) by irradiation for 1 hr. in a neutron flux of 10¹³ per sq. cm per sec.; the sensitivity on a 20-mg sample is 0.002 p.p.m. After irradiation for two weeks, In may be determined with the same accuracy by the activity of ¹¹⁴In in a 400-mg sample. The irradiated sample is fused with Na₂O₂ and In is pptd. from the melt as In(OH)₃ with inactive In as carrier, and is then extracted with diethyl ether from 4.5 M HBr. After separation from Fe by normal chemical methods, In is pptd. as the 8-hydroxyquinoline complex, the ppt. is weighed and the activity measured. The content of In is calculated by comparison with a similarly treated sample of known indium content. By this method, 0.025 p.p.m. of In was found in granite and 0.065 p.p.m. in diabase. The determination of In in cylindrite ($\approx 0.15\%$ of In)

was also carried out by a direct measurement of the activity after irradiation for 1 sec., with a correction for the activity of the relatively long-lived isotopes of Sb and Sn; the results agree well with those of the chemical method when the In is separated from accompanying metals.

C. D. KOPKIN

415. Rapid colorimetric determination of large amounts of thallium. S. M. Milaev. *Sb. Nauch. Trud. Vses. Nauch.-Issled. Gorno-Metallurg. Inst. Tsvet. Met.*, 1958, (3), 258-265; *Ref. Zhur. Khim.*, 1959, (10), Abstr. No. 34,604.—It is shown that the photometric method in which methyl violet (I) is used (*Ref. Zhur. Khim.*, 1956, Abstr. No. 4155) may be applied to the determination of large amounts of Tl if benzene instead of toluene is used as a solvent for the complex of $TlCl_4^-$ with I. The spectral characteristics of the benzene and toluene soln. of the Tl-I complex are identical (max. absorption 530 to 620 $\mu\mu$), but the solubility of the complex in benzene is considerably higher (to extract 100 μg of Tl one extraction with 10 ml of benzene is sufficient, while 10 ml of toluene quantitatively extracts only 30 μg of Tl); this widens the concn. range in which Beer's law is obeyed. As a result of testing known methods for the separation of Tl from Sb, it is established that the best is the extraction of thallium bromide with diethyl ether. For the determination of Tl in the various materials of thallium production, two procedures suitable for process control are described—(i) with preliminary removal of Sb for materials with a Tl to Sb ratio <100:1 and a content of Tl of 0.5 to 3%, and (ii) without removal of Sb for materials with a Tl to Sb ratio >100:1 and a content of Tl of 0.5 to 50%. The relative error of the determination, as compared with the usual gravimetric methods, is >4%. C. D. KOPKIN

416. Cerimetric determination of thallium(I). K. Bhaskara Rao and G. Jagga Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, **188** (2), 83-86 (in English).—The determination of Tl^+ by direct titration with $Ce(SO_4)_2$ soln. has been studied. The reaction is catalysed by ICl (I) and the titration can be carried out in 2 N HCl at 50° in the presence of 1 ml of 0.005 M I per 50 ml of total vol., with ferroin as indicator. The indicator is affected if the acid concn. is >3.0 N. The end-point may be determined potentiometrically if the titration is carried out at room temperature in N HCl in the presence of 5 ml of 0.005 M I. Higher acid concn. reduce the potential break at the end-point.

S. M. MARSH

417. Identification of scandium. R. Vanossi. *An. Asoc. Quim. Argentina*, 1958, **46** (4), 291-309.—The method is based on the formation of a blue ppt. with carminic acid. The sensitivity is increased in the presence of $BaSO_4$ carrier. *Procedure*—Neutralise the soln. of the metal in H_2SO_4 (4 to 5 ml) with 5 N NaOH and make it 0.30 to 0.35 N in acetic acid. Boil, and add 0.5% carminic acid soln. (0.2 ml). Add 1 drop of 0.5 M $BaCl_2$, stir, and centrifuge, and wash the ppt. with water (1 ml). A blue or blue-violet colour in the ppt. indicates the presence of Sc. Other elements interfere and a general scheme is given for their prior separation, thus enabling 1 μg of Sc to be detected in the presence of 10 mg or more of any other element.

E. C. APLING

418. Use of trihydroxyfluorone derivatives in photometric analysis. Determination of scandium. E. A. Biryuk and V. A. Nazarenko (Inst. Gen. and

Inorg. Chem., Ukrains. Acad. Sci., Odessa). *Zhur. Anal. Khim.*, 1959, **14** (3), 298-302.—Derivatives of 2:3:7-trihydroxy-6-fluorone are the most sensitive of the α -hydroxyquinone compounds giving colour reactions with Sc; the 9-propyl derivative can be used to detect Sc at a dilution of 1 in 5×10^3 and to determine 0.04 to 2 μg of Sc per ml. Soln. of Sc complexes obey Beer's law. *Procedure*—Use a test soln. (1 to 10 ml) (>0.005 N in acid) which after dilution to 25 ml has a concn. in the range of $1 \times 10^{-6} M$ (0.045 μg of Sc per ml) to $8 \times 10^{-6} M$. Add 1% gelatin soln. (0.5 ml) and 0.003% 9-propyl-2:3:7-trihydroxy-6-fluorone soln. (5 ml), dilute to 25 ml with an acetate buffer at pH 5.6, and set aside for 10 min. Measure the extinction at 530 $\mu\mu$ against a blank. K. R. C.

419. The reaction between cerium(IV) ions and peroxysulphuric acid. L. J. Csányi, F. Solymosi and J. Szűcs (Univ. Szeged, Hungary). *Naturwissenschaften*, 1959, **46** (10), 353 (in English).—In the titration of a soln. containing H_2O_2 and H_2SO_4 an error occurs which is dependent on the rate of addition of $Ce(SO_4)_2$, and is ascribed to the reaction of H_2SO_4 with Ce^{4+} with evolution of O. The reaction is not stoichiometric, and its rate is strongly influenced by the nature and concn. of the anion if other cerium salts are used, and also by the addition of Ce^{4+} . G. BURGER

420. Selective gravimetric method of determination of cerium in rare-earth oxides. E. Negrusz (Inst. of Inorg. Chem., Gliwice, Poland). *Chem. Anal.*, Warsaw, 1958, **3** (5-6), 813-816.—Cerium is ptd. as iodate from a soln. of rare-earth-metal nitrates after oxidation with $KBrO_3$, and weighed as CeO_3 after conversion into the oxalate and ignition. H. DMOWSKA

421. Colorimetric determination of cerium(IV) in the presence of iron(III) and lanthanum(III) with o-dianisidine. G. Popa, D. Negoiu and G. Baiulescu (Lab. f. anorg. u. anal. Chem., Univ., "C.I. Parhon," Bucharest, Romania). *Z. anal. Chem.*, 1959, **167** (5), 329-331.—In 20% H_2SO_4 , Ce^{IV} gives a red colour with o-dianisidine (I), with maximum extinction at $\approx 469 \mu\mu$. To the test soln. is added 2 ml of 0.05% I in ethanol and the whole is diluted to 10 ml, to give a final concn. of 20% of H_2SO_4 . Beer's law is obeyed for up to 100 μg of Ce per 10 ml. Interference from Fe^{III} up to a max. ratio of Fe to Ce of 800:1 is eliminated by the addition of H_3PO_4 . Tervalent La does not show any interference for ratios of La to Ce up to 50:1. Similar ratios could be expected to apply for Pr^{III} , Nd^{III} and Er^{III} . T. R. ANDREW

422. Modification of the colorimetric analysis for silica according to the method of Gettler and Umlberger. M. D. Appleton and R. J. Burns (Univ., Scranton, Pa.). *Proc. Pa. Acad. Sci.*, 1958, **32**, 69-73.—A modification of an earlier method for determining Si in tissue is described. Dissolve a melt of SiO_2 in Na_2CO_3 - K_2CO_3 in boiling water, dilute to 600 ml, acidify with excess of acetic acid and expel CO_2 by boiling. To the cool soln. add 13% $(NH_4)_2MoO_4$ soln. (20 ml) and after 20 min. add 10% oxalic acid soln. (20 ml). After a further 10 min. add 10 ml of a soln. prepared by treating 0.84 g of benzidine hydrochloride with a few drops of 95% ethanol and 100 ml of 10% $NaHSO_3$ soln., boil for 0.5 hr., cool and read at 520 $\mu\mu$. The soln. may be diluted after, instead of before, the colour development. The procedure was tested on pure SiO_2 .

CHEM. ABSTR.

423. Spectrophotometric determination of silica in the presence of fluorine and phosphorus. S. Greenfield [Res. Dept., Albright & Wilson (Mfg) Ltd., Oldbury, Birmingham, England]. *Analyst*, 1959, **84**, 380-385.—The sample is fused with Na_2CO_3 and Na_2O_2 , the melt is dissolved in water, acidified with HCl, diluted to 250 ml and stored in a polyethylene bottle. A 20-ml aliquot is added to 50 ml of 1% (w/v) aq. ammonium molybdate soln. and the mixture is set aside for 5 min. \pm 5 sec. at $20^\circ \pm 1^\circ$. From a burette 60 ml of 50% (v/v) HCl is added, and the well-mixed liquid is set aside for 10 min. \pm 5 sec. at $20^\circ \pm 1^\circ$. A 1% SnCl_2 soln. (10 ml) is added and the mixture is again set aside for 5 min. \pm 5 sec. at $20^\circ \pm 1^\circ$. A compensating soln. is prepared by adding 60 ml of 50% HCl to 50 ml of 1% aq. ammonium molybdate soln., SnCl_2 is added and the mixture is set aside for 20 \pm 1 min. at $20^\circ \pm 1^\circ$. The extinction of the sample soln. is measured against the compensating soln. at 800 μm , and the amount of SiO_2 is determined by means of a calibration graph.

A. O. JONES

424. Determination of free silica in the presence of silicates with pyrophosphoric acid. A. I. Bulycheva and P. A. Mel'nikova. Symposium: Determination of free silica in rocks and ore dust. Moscow. *Akad. Nauk SSSR*, 1958, 23-32; *Ref. Zhur., Khim.*, 1959, (11), Abstr. No. 38,328.—In this simplified determination, the platinum crucibles are replaced by quartz crucibles to avoid attack by $\text{H}_4\text{P}_2\text{O}_7$ (I), and crystalline I (m.p. 61°) is used instead of H_4PO_4 . *Procedure*—Grind 0.1 g of sample, dry it at 105° to 110°, ignite in a quartz crucible at a clear red heat for 30 min. and cool; add 5 ml of conc. HCl, heat (but not to boiling-point) for 10 min., add 5 ml of water, heat to boiling-point, filter, and wash the residue with hot (90°) HCl (1:9) (2 \times 5 ml) and then with hot water till free from Cl^- . Dry the filter and residue in a quartz crucible, ash, ignite and add 5 g of I. Heat at $250^\circ \pm 3^\circ$ for 12 min., transfer the contents of the crucible to a beaker with 20 to 40 ml of water (heated to 60° or 70°) and filter with suction on an ashless paper. Wash the residue, dry, ignite and weigh. Carry out a blank concurrently. The results from synthetic mixtures agree well with those of other methods, with the exception of the thermal method, which gives much lower results.

C. D. KOPKIN

425. New method for determining free silica in the presence of silicates. N. G. Polezhaev. Symposium: Determination of free silica in rocks and ore dust. Moscow. *Akad. Nauk SSSR*, 1958, 33-43; *Ref. Zhur., Khim.*, 1959, (10), Abstr. No. 34,620.—This rapid method is based on the conversion of the SiO_2 into the soluble state by fusion with a mixture of KHCO_3 and KCl. On subsequent leaching of the melt with Na_2CO_3 soln., the combined SiO_2 separates as an insol. residue, and SiO_2 in the soln. is determined photometrically as the molybdate-silico heteropoly acid. The flux, prepared by carefully grinding equal amounts of anhyd. KCl and KHCO_3 (the homogeneity being tested by titrating 1 g of the mixture with N HCl) is used in 50 times the amount of sample. To remove non-silicate compounds of Fe, Mg, Ca, etc., dissolve 0.05 g of sample by boiling for \approx 2 min. with 10 ml of a mixture (1:1) of HCl and HNO_3 , cool, filter, wash the residue successively with hot soln. of 2% NH_4Cl (2 \times 10 ml) and 10% Na_2CO_3 (2 \times 10 ml), then ignite in a steel crucible and fuse with 2.5 g of the flux, keeping the melt in the liquid state for

2 or 3 min. Leach the melt with 5% Na_2CO_3 soln. (40 ml), heating the mixture to boiling after each addition of the soln. Filter the resulting soln. make up to 60 ml, and determine the Si photometrically. To determine amorphous SiO_2 , treat 0.05 g of the sample in a metal crucible with 4% KOH soln. (15 ml), boil for 3 to 5 min., filter, wash the residue first with a 20% soln. of the flux (12 ml) and then with 2% KOH soln. (10 ml), make the filtrate up to 60 ml, and determine Si photometrically.

C. D. KOPKIN

426. Determination of quartz in the presence of silicates by a kinetic method. A. N. Il'in. Symposium: Determination of free silica in rocks and ore dust. Moscow. *Akad. Nauk SSSR*, 1958, 72-77; *Ref. Zhur., Khim.*, 1959, (11), Abstr. No. 38,329.—Ignite the sample (10 to 100 mg) in a quartz crucible at 900° for 20 min. to remove organic matter and water; cool, add Na_2SiF_6 (0.4 g), mix carefully, add H_4PO_4 (6 ml) that has been heated to 250° and again cooled to room temp., and place in an autoclave, which is heated at between 260° and 270° for 30 min. At the increased temp. in the phosphate medium the silicates decompose with the formation of SiF_4 ; quartz remains insoluble under these conditions. Cool the autoclave in air to 120° or 130° in 8 to 10 min., and pour the contents of the crucible into boiling water and filter the soln. Wash the residue on the filter with hot water till neutral to litmus, dry it in a platinum crucible, ignite and weigh. Moisten the residue with water (0.5 to 1 ml), add 2 or 3 drops of H_2SO_4 and 5 ml of 40% HF, and evaporate to dryness on a sand bath. Again ignite the crucible and re-weigh. The difference between the two weights gives the amount of quartz.

C. D. KOPKIN

427. Polarographic determination of germanium in coal ash. M. Węcławska and G. Popanda (Mining Inst., Katowice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 889-891.—The polarographic determination of Ge in coal ash and flue dust is described. The minimum detectable concn. is 0.5 μg per ml. The polarograms are compared with those of standard soln. The results compare well with those obtained by spectrometric and spectrographic methods.

H. DMOWSKA

428. Spectrographic determination of traces of germanium dioxide in brown-coal ash. Z. Gregorowicz (Inorg. Chem. Dept., Silesian Tech. Inst., Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 777-782.—Germanium dioxide (0.0003 to 0.03%) in brown-coal ash is determined spectrographically. An auxiliary copper electrode containing 0.1% of Ni provides the 3050-82-A Ni line as standard.

H. DMOWSKA

429. Occurrence and determination of germanium in coal ash from power plants. R. C. Corey, J. W. Myers, C. H. Schwartz, F. H. Gibson and P. J. Colbassani (U.S. Bur. Mines, Region V, Pittsburgh, Pa.). *U.S. Bur. Mines, Bull. No. 575*, 1959, 68 pp.—The concn. of Ge in numerous samples of coal and ash and in various waste materials has been determined. Methods of ashing samples, to avoid loss of Ge by volatilisation, are discussed and the procedure adopted, based on a method developed by the Eagle-Picher Co., together with the spectrographic determination of Ge, are described. The lower limit at which Ge can be determined quantitatively by spectrographic analysis is 50 p.p.m.

but concn. < 20 p.p.m. can be detected qualitatively. For materials containing > 1000 p.p.m. of Ge a gravimetric procedure (Eagle-Picher standard method 250) was used in which the sample is digested with acid, the Ge is separated by distillation as GeCl_4 , followed by pptn. as GeS . The ppt. is ignited and weighed as GeO_2 . To recover Ge retained in the insol. residue from the acid treatment, this residue is fused with NaOH , the melt is acidified, and the Ge is separated as GeCl_4 . For samples containing < 50 p.p.m. of Ge, spectrographic analysis was supplemented by a modified form of the phenylfluorone colorimetric method (cf. Cluley, *Analyst*, 1951, **76**, 517). By this procedure as little as 20 p.p.m. of Ge can be determined in a 0.2-g sample of coal ash. Results obtained in co-operative tests, by using all 3 methods, are compared.

J. M. JACOBS

430. Quantitative spectral analysis of germanium and indium in ores. J. Buzincu and M. Petrescu. *Rev. Met., Acad. R.P.R.*, 1958, **3** (3), 109-118 (in English).—The advantages of complete volatilisation are discussed; the ore is contained in the cavity of the carbon anode and a d.c. arc (9 amp.) is used. The apparatus employed and the dimensions of the carbon electrodes are given. The determination of Ge in a copper ore and In in a zinc ore are given as examples and comparison is made with known standard samples (Ge 0.005, 0.01, 0.05 and 0.08%; In 0.01, 0.1, 0.5 and 1.0%). With Ge the max. error was 7.4%; with In 9.0%.

S.C.I. ABSTR.

431. Spectrographic determination of tin in type metal. D. D. Lazebnik and V. I. Yatsenko. *Nauch. Zap. Ukr. Polig. Inst.*, 1958, **12** (1), 99-102; *Ref. Zhur., Khim.*, 1959, (3), Abstr. No. 7986.—The analysis is carried out with the steetoscope SL-3 by the electric spark transfer method (Sventitskii and Taganov, *Zavod. Lab.*, 1949, **13**, 850). Prepare standards by alloying tin, lead and antimony in graphite crucibles under a flux. Heat the molten lead to 500° , add the antimony, and then the tin at 400° . The transfer of the test material to a copper electrode is effected by a generator discharge in a transformer circuit working at 1.5 amp. (Ref. *Zhur., Khim.*, 1959, Abstr. No. 8049). The transfer takes 10 sec.; the electrode gap is 0.5 mm. The generator is connected to an interrupter. Excite the spectra by using copper electrodes in an a.c. arc discharge at 2.5 amp. and discharge gap 1 mm. The concn. of Sn is found by using the lines Sn 5631.6 and Cu 5641.3 and reference to a rectilinear calibration curve on the co-ordinates C and t , where C is the concn. of Sn and t is the duration of visibility of the Sn lines. The determination takes 4 to 5 min.; the error is $\pm 5\%$.

C. D. KOPKIN

432. Spectrophotometric determination of small quantities of lead in aluminium and copper alloys, in iron and steel and similar materials. J. F. W. Tertoolen, D. A. Detmar and C. Buijze (Inst. for Anal. Chem., Rijswijk, Holland). *Z. anal. Chem.*, 1959, **167** (6), 401-408.—Lead is extracted from soln. as the diethyldithiocarbamate (I) complex, which is then treated with CuSO_4 soln. to convert it into the blue Cu complex, and measured spectrophotometrically. With an aluminium alloy containing $> 0.01\%$ of Pb, a 200-mg sample is heated in NaOH soln. (25%) (10 to 15 ml) and acidified with HNO_3 (7 N, 6 ml in excess) (Si and Mg may cause turbidity here). Sodium citrate soln. (10%) (20 ml) and K Na tartrate soln. (30%) (30 ml) are

added and the soln. is made alkaline by the addition of 25% NaOH soln. (10 ml in excess) and warmed till clear. After oxidation with satd. bromine water (10 ml), 20% KCN soln. (10 ml), I soln. (1% of the Na salt, filtered and stored in a brown glass container) (7.5 ml) and 10 ml of CCl_4 are added to the soln., which is then shaken and allowed to separate. The aq. layer is re-washed with 5 ml of CCl_4 and the combined organic layers are shaken with 5% CuSO_4 soln. (2 ml) for 3 min. After the aq. layer has been washed with a further 2 ml of CCl_4 the organic layer is made up to 25 ml and measured at 435 m μ . The removal of interfering Bi is described. Copper alloys are treated similarly after initial dissolution in HNO_3 (or, in the presence of Sn, in aqua regia). A larger sample and slightly modified procedure will enable alloys containing 0.01 to 0.001% of Pb to be analysed. A similar technique is employed with iron and steel ($> 0.01\%$ of Pb), and other materials.

E. G. CUMMINS

433. Polarographic determination of lead in Perhydrol, hydrofluoric acid and ammonium fluoride. W. Kemula and J. Kornacki (Dept. of Inorg. Chem., Warsaw Univ., Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 825-830.—After a preliminary thermal decomposition of the sample, Pb is determined polarographically in 30% H_2O_2 in concn. $\approx 0.002\%$ and in HF and NH_4F in concn. $\approx 0.01\%$. In a soln. containing 10% of ethanol and 0.1 M in NH_4NO_3 and HNO_3 , a well-shaped Pb^{2+} wave is obtained. Limits for interfering cations and anions are given.

H. DMOWSKA

434. Simultaneous polarographic determination of lead and zinc in sulphide ores. J. Zaremba (Inst. of Inorg. Chem., Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 845-848.—Lead ($\approx 2\%$) and Zn ($\approx 6\%$) in sulphide ores are determined simultaneously by a polarographic method. The interference of Fe is removed by the addition of hydroxyammonium chloride; Cu, Cd, Ni and Co do not interfere. Potassium chloride (0.1 N) is used as basal solution with a 0.1% aq. soln. of acid fuchsin as a maximum suppressor.

H. DMOWSKA

435. Determination of oxygen and hydrogen in titanium. II. Influence of various factors on the precision and accuracy of the determination by the vacuum fusion method. Nakaaki Oda, Noboru Katayama and Kazue Endo (Takaoka Plant, Nippon Soda Co., Takaoka, Toyama-ken). *J. Japan Inst. Metals, Sendai*, 1958, **22** (8), 408-412.—The temp. and the grain size of the graphite appear to be the most important factors, the optimum being 1920° to 1950° and 18 to 20 mesh, respectively. Gas removal from the crucible and the graphite is achieved at 2300° within 4 hr., and from the sample within 40 min. under the optimum conditions. The influence of solidification due to the formation of titanium carbide and that of the getter action of the evaporated film of Al and Ca decrease the rate of extraction of the gas, but are eliminated by an acid treatment of the graphite. Chlorine in the sample forms MgCl_2 , but does not cause interference. The error is $\approx 5\%$ for 0.01% of O, and $\approx 8\%$ for 0.01% of H.

K. SAITO

436. Determination of iron in metallic titanium with acridine. Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku, Tokyo). *J. Japan Inst. Metals, Sendai*, 1958, **22**, (3), 130-132.—Ferric iron (< 20 mg) is pptd. from H_2SO_4 soln. ($< N$) in

the presence of NH_4SCN soln. (50%) (10 ml) and acridine (5% in ethanol) (10 ml). The ppt. readily dissolves in acetone containing ammonium acetate and is titrated with EDTA at pH 2 to 3. Cobalt, Zn, V, Mo^{V} and Mo^{VI} are co-ppptd., but do not react with EDTA at pH 2 to 3. *Procedure*—Dissolve the sample (1 g) in H_2SO_4 (20 ml) and HNO_3 (10 ml), heat to white fumes, then dissolve the residue in water (50 ml) and make up to 100 ml. Dilute an aliquot (10 to 50 ml) to 0.5 to 1 N with respect to H_2SO_4 and precipitate Fe as described above. Dissolve the ppt. in ammonium acetate soln. (50%) (5 ml) and acetone (20 ml), adjust the pH and titrate with EDTA soln. (1%) until a red colour appears.

K. SAITO

437. Quantitative spectrochemical determination of silicon and vanadium in titanium tetrachloride. Nakaaki Oda, Sadayuki Tsunoo and Toshio Hashimoto (Takaoka Plant, Nippon Soda Co., Takaoka, Toyama-ken). *J. Japan Inst. Metals, Sendai*, 1958, **22** (9), 468-472.—Titanium chloride (≈ 2.5 ml) is transferred from an ice-cooled container into HCl (1:1) (10 ml) with a syringe and the soln. (0.4 ml) is allowed to soak into a porous carbon electrode (diam. 3 mm; preliminary discharge, 10 amp., 10 sec.), which is used for arc excitation (200 V, 12 amp.; arc gap, 6 mm; exposure, 20 sec.). By the use of the line pairs Si 2516-12-Ti 2822-16 and V 3092-72-Ti 2641-1 Å, 0.001 to 0.1% of Si and 0.008 to 0.3% of V can be determined with a coeff. of variation of $\pm 9\%$.

K. SAITO

438. Analytical chemistry of zirconium. New gravimetric method for the determination of zirconium. P. Spacu and F. Popa. *An. Univ. "C. I. Parhon" Bucureşti, Ser. Științ. Nat.*, 1958, (17), 45-53.—The sodium or ammonium salt of mercaptobenzothiazole (I) is added to a soln. of Zr in HNO_3 until the pH of the soln. is 6 to 7.6 (bromothymol blue). The ppt. is filtered off immediately and washed with water but, as it is discoloured by small amounts of I and $\text{Zr}(\text{OH})_4$, it must be converted into ZrO_2 and weighed. This method is easy to perform and differences found are > 0.0002 g. Alkali-metal, ammonium, strontium and magnesium salts do not interfere.

C. A. BLAU

439. Quantitative spectrographic determination of zirconium in minerals. M. Roca Adell, F. Alvarez Gonzalez and R. Fernandez Cellini (Chem. Div., Assembly of Nuclear Energy, Madrid). *An. Real Soc. Esp. Fis. Quim. B*, 1958, **54**, 273-277.—A method is described for the analysis of minerals containing 0.6 to 55% of ZrO_2 . Cobalt is used as the internal standard for low-grade ores and Cu for high concn., with GeO_2 as diluent. The line pairs employed are, respectively, Zr 2571.4-Cu 2585.3 and Zr 2571.4-Cu 2768.9. A 10-amp. d.c. arc is used. The method is semi-quant., with deviations of $\pm 7.7\%$ on ores containing up to 8% of ZrO_2 .

W. R. O'NEILL

440. Photometric determination of zirconium in phosphorites with catechol violet. Yu. A. Chernikhov, W. F. Luk'y'anov and E. M. Knyazeva. *Zhur. Anal. Khim.*, 1959, **14** (2), 207-210.—*Procedure*—Dissolve the sample (70 µg of Zr) in conc. HCl (5 ml), evaporate on a sand bath to ≈ 0.5 ml, then dilute to 50 ml. Add 0.05 M EDTA (1 ml), neutralise with aq. NH_3 and then make the soln. slightly acid to methyl orange. Add acetate buffer soln. (15 to 20 ml) to bring the pH to 5.2 to

5.4, and 0.001 M catechol violet (4 ml) to develop the colour, and read the extinction at $620 \text{ m}\mu$ against a reagent blank. Refer the results to a calibration curve. Soln. of the Zr complex obey Beer's law; 5 to 70 µg of Zr can be determined.

K. R. C.

441. The determination of oxygen in metallic zirconium by the vacuum fusion and the bromination-carbon reduction methods. Yasumoto Otake (Copper Refinery, Sumitomo Metal Ind.). *J. Japan Inst. Metals, Sendai*, 1958, **22** (7), 341-345.—For the determination of O (0.01 to 0.15%) in zirconium by the vacuum fusion method (Sloman, *Iron and Steel Inst. Special Rep.*, 1937, No. 16, 96; Guldner and Breach, *Anal. Chem.*, 1950, **22**, 366), the addition of tin (0.1 to 0.2 g for 0.1 g of the sample) decreases the time (≈ 30 min.) taken for extraction of O at 1850° . The bromination method (Codell and Norwitz, *Anal. Chem.*, 1956, **28**, 2006) is largely affected by the time of heating; with a 0.5-g sample at 925° , the flow of Br must be continued for 120 min. after the yellow fumes of ZrBr_4 disappear from the vertical tube.

K. SAITO

442. Activation analysis by short-life nuclides. I. Determination of hafnium in zirconium by hafnium-179m. Toshio Nakai, Seishi Yajima, Isao Fujii and Minoru Okada (Japan Atomic Energy Res. Inst., Tokai, Ibaragi-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (1), 49-52.—The experimental conditions for the neutron activation analysis of Hf (<100 p.p.m.) were studied with a water-boiler type of reactor (neutron flux, 10^{11} per sq. cm per sec.). The sample (<100 mg) is irradiated for 1 min. and the photo-electron peak of ^{179m}Hf (0.215 MeV) is measured after 10 sec., with a γ -ray scintillation spectrometer (NaI crystal) for 10 sec. The coeff. of variation is <2% for 5 to 20 µg of Hf. The ^{80}Zr simultaneously produced (half-life 0.83 sec.) decays completely during the 10-sec. cooling period.

K. SAITO

443. Separation of a trace amount of hafnium from zirconium with cation-exchange resin. Yoshiro Hoshino (Res. Lab. of Resources Utilisation, Tokyo Inst. of Tech., Meguro-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (4), 393-396.—The separation of Hf (<0.2 mg) from Zr (>500 mg) in one operation, with Amberlite IR-120 (H) and dil. H_2SO_4 as eluent is unsatisfactory. The Hf can, however, be concentrated to 1 to 10% of the Zr by eluting with 8 N H_2SO_4 (600 ml) and 1.2 N H_2SO_4 (250 ml) (rate of flow, 100 ml per hr.) from a column (1.5 cm \times 50 cm) of the resin (100 to 150 mesh). The 1.2 N H_2SO_4 eluate is treated with FeCl_3 soln. (1 mg of Fe per ml) (2 to 5 ml) and 8 N aq. NH_3 ; the ppt. is dissolved in 8 N HNO_3 (5 ml), diluted to 20 ml and passed through a second column (1 cm \times 26 cm). The column is then eluted with 8 N H_2SO_4 at a flow rate of 25 ml per hr. The first 75-ml portion is discarded, and the following 80-ml portion is collected; almost all the Hf is recovered in this fraction free from Zr. The Fe is not eluted.

K. SAITO

444. Spectrographic determination of small amounts of hafnium dioxide in zirconium dioxide. S. M. Solodovnik and A. I. Kondrashina (State Sci.-Res. Inst. of Rare and Trace Metals, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (2), 248-249.—A self-collimating spectrograph with a single lens condenser is used. The ZrO_2 (20 mg) is mixed with charcoal powder (10 mg) and the mixture packed into a crater (2 mm diam. \times 5 mm deep) in the

graphite anode. The upper graphite electrode is tapered. The arc is fed by a 10-amp. current, the slit width is 0.01 mm and the exposure time 2 min. The spectrum is obtained by super-imposing two exposures (with two samples) on the same area of the photographic plate (type I). The results are obtained by reference to a calibration curve with the lines Hf II 2641.4 and Zr 2626.0. The error of a single determination of 0.003 to 0.03% of Hf is $\pm 30\%$; with $>0.03\%$ of Hf it may be $\pm 10\%$.

K. R. C.

445. Microchemical detection of thorium with alizarin red S in the presence of anion-exchange resin. Kiyoshi Kato and Hidetake Kakihana (Municipal Tech. High Sch., Kita-cho, Nakamura-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (2), 169-171.—The limit of detection of Th with alizarin red S (C.I. Mordant Red 3) (**I**) is reduced to 0.03 μg (limiting dilution 1 in 1×10^{-4}) by the presence of a particle of Dowex 1-X1 resin at pH 3.4 to 3.8. The detection is facilitated by the use of resin impregnated with 0.01% **I** in aq. ethanol (1:1). The sample (one drop) is mixed with one drop each of 0.2 M K H phthalate and 0.03 N NaOH on a spot-plate; the resin particle is added and the colour observed after 3 hr. Vanadium, Mo, W, Ge, Fe^{III}, Sn, Cr, Ca, F, PO_4^{2-} and oxalate interfere.

K. SAITO

446. Analytical aspects of some organic acids. III. Gravimetric determination of thorium by *m*-phenylenedioxycydiacetic acid. C. S. Pande and T. S. Srivastava (Chem. Dept., Lucknow Univ., India). *Z. anal. Chem.*, 1959, **187** (5), 332-335 (in English).—Thorium is quant. ptd. by *m*-phenylenedioxycydiacetic acid within the pH range 4.0 to 5.4 as a ppt. of variable composition which gives ThO_2 on ignition. The separation from Be^{2+} , Mg^{2+} , Ca^{2+} , Zn^{2+} , Pb^{2+} and Mn^{2+} is effected in a single pptn., but a double pptn. is necessary to separate Th from Al^{3+} , UO_4^{2-} and lanthanides; ZrO^{2+} are separated by pptn. from 0.1 N HNO_3 . Ti^{4+} are masked with chromotropic acid, and Fe^{2+} must be reduced to Fe^{2+} with hydroxyammonium sulphate; Sn^{2+} , Sn^{4+} and Cr^{3+} interfere. Recoveries of 2 to 60 mg of added Th are within 0.1 mg of theoretical values.

T. R. ANDREW

447. New rapid method for the determination of thorium in the presence of zirconium, iron, lanthanum, uranium and other heavy metals. R. Pfibl and K. Burger (Res. Inst., Czech. Acad. Sci., Prague). *Magyar Kém. Foly.*, 1959, **65** (5), 204-206.—At pH < 1, the complex of EDTA (**I**) with Th is decomposed by SO_4^{2-} and the liberated **I** is titrated with $\text{Bi}(\text{NO}_3)_3$ soln. *Procedure*—To the soln. containing Th (5 to 30 mg) add 0.05 M or 0.1 M **I** (10 to 20 ml, according to the Zr or Fe^{2+} content of the soln.). With 2 N aq. NH_3 adjust the pH to between 2 and 3.5 (indicator paper). Add Xylenol orange as indicator (3 to 4 drops) and back-titrate the excess of **I** with 0.05 M or 0.1 M $\text{Bi}(\text{NO}_3)_3$, keeping the pH between 2 and 3.5 with 2 N aq. NH_3 . The colour changes from yellow to reddish-violet, or to orange if Fe^{2+} are present. When the pH has finally been adjusted, carefully re-adjust the end-point with 0.01 M **I** or $\text{Bi}(\text{NO}_3)_3$. Add anhyd. Na_2SO_4 (1 g) and 2 N HNO_3 (1 to 1.5 ml) and titrate the liberated **I** with 0.01 M $\text{Bi}(\text{NO}_3)_3$. If the yellow colour changes to orange, acidify with a few drops of 2 N HNO_3 . The colour change is from yellow to reddish-violet. The accuracy is within $\pm 1\%$. If the amount of Co^{2+} or Ni^{2+}

present is 10 to 20% of that of the Th, they do not interfere if at the decomposition stage the pH is <3 ; La^{3+} , UO_4^{2-} , Mg^{2+} , Mn^{2+} , Zr^{4+} and Fe^{2+} do not interfere. The end-point is not clear if Fe^{2+} are present; in this case, oxidise the Fe^{2+} with KMnO_4 to Fe^{3+} and destroy the excess of KMnO_4 with H_2O_2 .

A. G. PETO

448. Determination of thorium in the presence of uranium, titanium and tungsten. H. H. Willard, A. W. Mosen and R. D. Gardner (Los Alamos Sci. Lab., N. Mex.). *U. S. Atomic Energy Comm. Rep. AECD-4282*, [1958], Decl. Dec., 1958, 10 pp.—Thorium is separated from U, Ti and W by pptn. as fluoride. The ppt. is ignited to the oxide, dissolved in HNO_3 , evaporated with HClO_4 , adjusted to pH 2 to 2.5 and titrated with EDTA (disodium salt), with Eriochrome cyanine R (C.I. Mordant Blue 3) as indicator. If <30 mg of Th is present, La is added as a carrier. *NUCL. SCI. ABSTR.*

449. Spectrographic analysis of nitrogen in metals. I. B. Borovskil, S. A. Skotnikov and I. F. Petrushin. *Trudы Inst. Metallurgii*, 1958, (3), 276-282; *Ref. Zhur. Khim.*, 1959, (14), Abstr. No. 49, 255.—Spectra are excited in a low-voltage spark discharge from a valve generator giving rectangular pulses with a frequency of 100 c/s. The scheme ensures a stable inter-electrode gap of 1 mm; the exposure time is 0.5 sec., regulated by means of a relay. The test samples are placed in the vacuum-chamber on a de-gassed copper electrode. The system is evacuated to 10^{-3} torr and then a N-free gas is admitted until the pressure exceeds atmospheric. With a capacity of 240 μF and self-inductance of 5 mH the N lines in the 4000-Å zone for standards containing 0.18% and 0.052% of N get into the over-exposure zone. In order to diminish the error arising from overheating if the quantity is small, the sample is embedded in lead or Wood's alloy. Analytical accuracy is adversely affected by elements forming unstable or volatile nitrides; the effect of such elements is considerable for steels alloyed with Si. The results of chemical and spectrographic determinations of common steels are in good agreement.

K. R. C.

450. Amperometric titrations with rotated platinum electrode. I. Determination of hydrazine by potassium bromate. Bharat R. Sant and Anil K. Mukherji (Univ., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (5), 476-480.—From 30 μg to 3 mg of hydrazine can be titrated amperometrically with 0.1 N KBrO_3 at an applied potential between zero and 0.3 V *vs.* the S.C.E. in the presence of 0.05 M KBr and 2 N HCl (or 1 to 5 N H_2SO_4). By titrating at a rotating platinum cathode, steady values of current are attained immediately, and the titration can be made in the presence of oxygen. By adjusting the concn. of BrO_3^- to $\simeq 10$ times that of hydrazine, a volume correction is unnecessary except for small volumes and precise work. The procedure is also applicable to phenylhydrazine, semicarbazide and similar compounds.

W. J. BAKER

451. Method of determining ammonia, cyanide, nitrite and nitrate when present together. E. Schulek, K. Burger and M. Fehér (Inst. f. anorg. u. anal. Chem., Budapest Univ.). *Z. anal. Chem.*, 1959, **187** (6), 423-429.—A micro-method for the determination of all four ions in the same sample is described. Ammonia and CN^- are distilled off at pH 8, and NH_3 is determined by titration of the

distillate, followed by the determination of CN^- by the BrCN - iodide reaction. In the residue in the distillation flask, NO_3^- are determined by reaction with KI in a stream of CO_2 (to remove NO) and titration with $\text{Na}_2\text{S}_2\text{O}_8$, followed by the reduction of NO_3^- by Devarda's alloy or Raney nickel, and titration of the NH_3 so formed. E. G. CUMMINS

452. New method for the determination of nitrates. I. Ya. Shaferstein, V. V. Bondar', S. I. Malakhova, A. T. Khamatova and E. A. Tsarevskaya. *Trudj Tadzh. S.-Kh. Inst.*, 1958, 1, 3-11; *Ref. Zhur., Khim.*, 1959, (9), Abstr. No. 31,035.—It is shown that in 0.75 N aq. NH_3 , NO_3^- are reduced to NO_2^- to the extent of 94-5% by shaking for 2 or 3 min. with zinc dust. On this basis a rapid and simple method is developed which is applicable to the analysis of soil, fertilisers, water, etc. To 5 ml of test soln. (pH 7 to 10) containing 0.01 to 10 mg of NO_3^- add 5 ml of 1.5 N aq. NH_3 and 0.1 g of zinc dust; shake vigorously for 2 to 3 min. and rapidly filter or centrifuge. The NO_2^- in an aliquot of the resulting soln. are determined photometrically with Griess - Illosvay reagent or by titration with permanganate. No interference is caused by Cl^- , SO_4^{2-} or urea; >1 mg of Mg and large amounts of Ca are first pptd. with NaF . Iron, Mn and other elements that interfere in the reduction of NO_3^- are pptd. with Na_2CO_3 . C. D. KOPKIN

453. New volumetric method for the indirect determination of phosphate with ethylenediaminetetra-acetate. K. Riedel (Wernerwerk f. Bauelemente der Siemens & Halske A.-G., München, Germany). *Z. anal. Chem.*, 1959, 188 (2), 106-112.—Phosphate, in dil. HClO_4 soln., is pptd. as bismuth phosphate with $\text{Bi}(\text{NO}_3)_3$ soln. and the excess of precipitant is titrated with EDTA (disodium salt) soln. The sample soln., which should contain >5 mg of PO_4^{3-} and no NO_3^- , is evaporated to dryness with 5 ml of conc. HNO_3 and the residue is dissolved in 13 ml of N HClO_4 and concentrated. After cooling, an excess (<7 ml) of 0.01 M $\text{Bi}(\text{NO}_3)_3$ is added, followed by 80 ml of boiling water and the mixture is heated to boiling, with constant stirring. A further 80 ml of water is added and the mixture is boiled for 5 min. The ppt. is allowed to settle and the mixture transferred to a wide-necked flask and made up to 300 ml with water. The excess of $\text{Bi}(\text{NO}_3)_3$ is titrated with 0.01 M EDTA after the addition of 5 drops of 0.1% aq. catechol violet soln. as indicator, which changes from blue through pink to orange - yellow at the end-point. Interference by Fe^{3+} is prevented by treating the HClO_4 soln. with 10 ml of reducing soln. (2 ml of \approx 50% hydrazine hydrate soln. diluted with 50 ml of water, neutralised with HClO_4 and made up to 100 ml with water) and 5 ml of water, and boiling for 10 min. before the addition of the $\text{Bi}(\text{NO}_3)_3$ soln. Chloride is removed as BiOCl during the dissolution with HClO_4 . Sulphate, Hg and Sb can be eliminated by simple pptn. reactions on the sample soln. Only In, Ga, Zr, Th and organic complex-formers interfere. S. M. MARSH

454. Volumetric determination of phosphate ions in the presence of calcium and other metal ions. E. Bakács-Polgár (Chem. Inst. d. Tierärztlich. Hochsch., Budapest). *Z. anal. Chem.*, 1959, 187 (5), 353-358.—Two procedures are presented for the vol. determination of \approx 40 mg of P_2O_5 in the presence of up to 20 mg of Ca^{2+} , 2.4 mg of Mg^{2+} , 2.7 mg of Al^{3+} , 11.2 mg of Fe^{3+} and 3.8 mg of F^- .

In the first method PO_4^{3-} are pptd. with Mg^{2+} in ammoniacal citrate soln., the ppt. is filtered off, dissolved in N HCl (10 ml), and neutralised to methyl orange with aq. NH_3 , and a slight excess of 0.1 M EDTA (disodium salt) is added. Buffer soln. [50 g of NH_4Cl and 400 ml of aq. NH_3 (sp. gr. 0.88) made up to 1 litre] (1 ml) is added, and a few drops of Eriochrome black T as indicator, and the excess of EDTA is titrated with 0.1 N MgCl_2 . Ethanol is then added to precipitate MgNH_4PO_4 and the soln. is titrated with 0.1 M MgCl_2 to a red-violet end-point. The alternative procedure involves adjustment to pH 3, complexing Al and Fe with an excess of disodium 1,2-diaminocyclohexanetetra-acetate, boiling, cooling and complexing Ca and Mg with EDTA (disodium salt). The determination is then completed as before.

T. R. ANDREW

455. Separation and determination of phosphate, silicate and arsenate. W. S. Clabaugh and A. Jackson. *J. Res. Nat. Bur. Stand.*, 1959, 62 (5), 201-205.—To the sample dissolved in H_2O (80 ml) is added 10% ammonium molybdate soln. (5 ml); HCl or aq. NH_3 is then added to bring the pH to about 4. After the addition of aq. Br and adjustment of the pH to 1.7 to 1.9 the soln. is boiled and diluted to 90 ml; HCl (10 ml) is then added and the P is extracted into diethyl ether (35 ml). The ether is washed with HCl (1:9) and after the addition of 2% SnCl_4 soln. (0.2 ml) and dilution to 25 ml the extinction is measured at 630 m μ . To the aq. phase is added HCl (10 ml) and the Si is extracted with n -butanol (50 ml), which is then washed with HCl (1:99) (3 \times 20 ml). After the addition of 2% SnCl_4 soln. (0.5 ml) and dilution to 50 ml, the extinction of the soln. at 630 m μ is measured. To the aq. phase is added aq. NH_3 (10 ml) and the As is extracted with isobutyl methyl ketone. The extract is washed with HCl (1:9) (3 \times 10 ml) and 10 ml of 0.04% SnCl_4 soln. After dilution of the ketone to 30 ml the extinction is measured at 630 m μ . The amounts of P, Si and As are derived from calibration curves. Extinctions of \approx 0.8 are recorded for about 32 μg of PO_4^{3-} , 31 μg of SiO_2 and 31 μg of As in the appropriate volumes of solvent. The extractions are unaffected by 1 g of various salts containing Cl^- , NO_3^- , SO_4^{2-} and ClO_4^- . G. J. HUNTER

456. Use of potassium manganate in quantitative analysis. III. Determination of antimony(III). G. den Boef and A. Daalder (Lab. Anal. Chem., Univ. of Amsterdam). *Z. anal. Chem.*, 1959, 167 (6), 430-431.—The accurate determination of Sb^{III} (>0.001 M) by oxidation with K_2MnO_4 in conc. NaOH soln. (0.5 to 4.0 M) is described.

E. G. CUMMINS

457. Colorimetric determination of bismuth in products of lead manufacture. L. N. Krasil'nikova. *Sb. Nauch. Trud. Vses. Nauch.-Issled. Inst. Gorno-Metallurg. Inst. Tsvet. Met.*, 1958, (3), 266-278; *Ref. Zhur., Khim.*, 1959, (10), Abstr. No. 34,622.—The photometric method with thiourea (*Anal. Abstr.*, 1956, 3, 3320) is used for the determination of Bi in all products of lead manufacture which contain 0.001 to 20% of Bi. Since the varying content of Sb and Fe (which interfere in the photometric determination) does not allow any one method to be used for their removal, the materials are divided into three groups—those with a relatively high content of Fe (6 to 30%) and a relatively low content of Sb (0.02 to 1.5%); those with a relatively low content of Fe (up to 6%) and a high

content of Sb (up to 12%); and those with relatively small amounts of Sb (from traces to 1.5%) and practically no Fe (from traces to 0.5%).

C. D. KOPKIN

458. **Polarographic determination of traces of bismuth in pure silver by the use of a mixture of sodium citrate and EDTA as supporting electrolyte.** Michihiro Ishibashi, Toyoshi Nagai, Taitiro Fujimaga and Wataru Funasaka (Dept. Ind. Chem. Fac. of Engng, Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1959, **8** (2), 107-110.—In 0.5 M Na citrate containing 0.01 M EDTA (pH 4.5) the $E_{1/2}$ values for Cu, Bi and Pb are -0.09, -0.64 and -1.1 V vs. the S.C.E., respectively. Bismuth ($\approx 10^{-6}$ %) in electrolytic silver (40 g) dissolved in HNO_3 is co-pptd. with $Al(OH)_3$ (0.2 mM) (Ishibashi *et al.*, *Anal. Abstr.*, 1959, **8**, 3403). After dissolution and re-pptn., the final ppt. is dissolved in HNO_3 . The soln. is evaporated to a syrup, 3 g of Na citrate and 1 ml of 0.2 M EDTA are added, the pH is adjusted to 4.5 with NaOH and the mixture diluted to 20 ml for polarography. The recovery of Bi is 77% and a correction factor is therefore applied. The error is $\approx 4\%$.
K. SAITO

459. **Separation of bismuth from mercury by the ammonia method.** A. Cygański (Dept. of Inorg. Chem., Technol. Inst., Łódź, Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 807-811.—Bismuth and Fe are separated from Hg by repeated pptn. with ammonium carbonate and ammonia from a soln. in HNO_3 . Mercury remains in soln. as ammonia complexes, and is pptd. from the filtrate by H_2S .
H. DMOWSKA

460. **Colorimetric titration of vanadium with alkaline ferricyanide.** S. V. Tatwadasi (Hindu Univ., Benares, India). *Z. anal. Chem.*, 1959, **188** (1), 15-17 (in English).—The gradual disappearance of the yellow colour of an alkaline $K_3Fe(CN)_6$ soln. during the addition of a vanadyl soln. has been utilised for the determination of either vanadium or ferricyanide. A Hilger Spekker Absorptiometer with a filter having max. transmission between 450 and 500 $m\mu$ was used. The results compare favourably with those by other standard procedures. The variation of the alkali concn. over a wide range does not affect the accuracy of the results, but if the titration is carried out by the reverse process of adding $Fe(CN)_6^{4-}$ to the vanadyl soln. the results are unreliable owing to the instability of quadrivalent V in the presence of alkali. S. M. MARSH

461. **Determination of vanadium in ferrovanadium.** B. E. Jaboulay. *Chim. Anal.*, 1959, **41** (5), 185.—**Procedure**—Decompose the sample (0.25 to 0.35 g) with H_2SO_4 (20 ml), HNO_3 (2 ml) and H_2O_2 (25 ml) at 100°. Add cold H_2O (100 ml) plus 0.1 N $KMnO_4$ in very slight excess; then add H_3PO_4 (d. 1.72) (5 ml) plus 4 or 5 drops of aq. Ba-diphenylaminosulphonate, and titrate the soln. with 0.1 N $FeSO_4$ to a green end-point (sharp). Calculate the percentage of V from the $KMnO_4$ equiv. of the vol. of $FeSO_4$ used after deducting 0.1 ml for the excess of $KMnO_4$ added initially. The method is rapid and accurate.
W. J. BAKER

462. **Determination of niobium in bismuth-base alloys.** U.K.A.E.A. (Res. Group, Woolwich Outstation, Royal Arsenal, London, S.E.18). AERE-AM 28, 1959, 4 pp.—The method is based on that of Ward and Marrazino (*Anal. Abstr.*, 1955, **2**, 3340). It is written with full details by F. E. Wild.

463. **Methods for concentrating niobium ions in natural waters.** N. A. Tyutina, V. B. Aleksovskii and A. D. Miller. *Trudy Leningr. Tekhnol. Inst. im. Lensoveta*, 1958, (48), 101-108; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,317.—Micro amounts of Nb are concentrated from a vol. of 1 litre by co-pptn. with organic reagents. On co-pptn. with tannin alone, 69% is separated; by using tannin with methylene blue, an average of 78%, and by using methylene blue with NH_4SCN , 72.5% is separated. A procedure is developed for co-pptg. Nb with $CaCO_3$ from a vol. of 1 to 2 litres; an average of 86% of the Nb is separated. The treatment of the ppt. is simple and rapid. This method of concentration has been successfully used under field conditions. The concentration of Nb has been carried out by extraction of the diethyldithiocarbamate complex of Nb. The optimum pH range (1.5 to 3.4) has been established in which 92% of the Nb (5 to 40 μ g of Nb_2O_5) is extracted. A procedure has been developed for determining Nb in the carbamate concentrates.
C. D. KOPKIN

464. **Galvanic analysis. Continuous determination of trace amounts of oxygen and hydrogen.** P. Hersch (10 Mountcastle Drive South, Edinburgh, Scotland). *Chim. Anal.*, 1959, **41** (5), 189-197.—The theory and practice of galvanic oximetry are given and the apparatus required for different applications is described and illustrated. The determination of small concn. of O by this method is based on the reaction—

$0.5O_2 + Pb + OH^- \rightarrow PbO_2H^-$

that occurs in the silver - KOH/lead cell, in which the silver-gauze cathode rests on a diaphragm [porous poly(vinyl chloride)] impregnated with KOH so that each wire is exposed to O on one side and to alkali on the other. Provided that the content of O in the in-flow gas is < 0.01 to 0.02%, the galvanic current recorded in the cell is proportional to the concn. of O and is $\approx 5 \mu A$ for 1 p.p.m. of O at a rate of flow of ≈ 100 ml per min. With a voltage of 60 to 120 and a variable resistance in circuit, the galvanic current is almost instantaneous and is stable during the measurements. The method is applicable to (i) the control of the purity of industrial O and of a protective atmosphere, (ii) the determination of O during the polymerisation of ethylene, (iii) the continuous measurement of O in boiler-feed water, and (iv) the determination of O in ≈ 0.1 ml of a biological fluid or of the O formed during photosynthesis. Hydrogen (e.g., in products of reduction or evolved during corrosion) can be determined indirectly after combustion in an excess of O, the initial and final vol. of which can be measured by the galvanic oximeter.
W. J. BAKER

465. **Separation and identification of peroxides by paper chromatography.** J. Cartilage and C. F. H. Tipper (Dept. of Inorg. and Phys. Chem., Univ. Liverpool). *Chem. & Ind.*, 1959, (26), 852-853.—The scheme described makes possible the separation of H_2O_2 , peroxy-acids, hydro-, dialkyl- and hydroxylalkyl-peroxides. By different pretreatment of the paper and the use of a variety of solvent mixtures, H_2O_2 can be identified, and characteristic R_F values obtained for other peroxides. A dil. soln. of o-tolidine and $(NH_4)_2SO_4$ - $FeSO_4$ in dil. acetic acid is a suitable spray reagent (blue spots with H_2O_2 , hydroperoxides and peroxy-acids), followed, after the spots have faded, by $Fe(SCN)_3$ for further colour development. The spots formed by dialkyl- and

hydroxyalkyl-peroxides develop only slowly with this reagent, but the process is speeded up by the addition of a 4% soln. of HI in acetic acid. Further confirmatory tests are described.

P. D. PARR-RICHARD

466. Analytical characteristics of commercial and purified sulphur. F. Fehér, S. Eckhard and K. H. Sauer (Chem. Inst., Univ. Köln, Germany). *Z. anal. Chem.*, 1959, **168** (2), 88-101.—A scheme for the complete analysis of the impurities in commercial and purified elementary sulphur is outlined. Carbon is determined by burning the sample in oxygen and observing the change in conductivity of dil. NaOH soln. as the combustion gases are bubbled through. The sample is first mixed with 10 times its amount of PbO₂ to fix 40 to 60% of the S as PbSO₄, and SO₂ is removed from the gases by an absorption tube containing H₂SO₄ and H₂O₂ at -50° followed by a tube containing Lewatit ion-exchange resin. Inorganic impurities are concentrated by combustion in a special apparatus and most of the elements present are determined qual. and quant. by spectrographic methods. Sodium and K in the combustion residue are determined by flame photometry. Phosphorus is determined by measuring the intensity of the orange colour produced with ammonium molybdate and ammonium vanadate in the presence of nitric acid. Halogens are determined by a spectrographic method (or photometrically for chlorine). The dissolved gases are extracted by melting the sample *in vacuo* and are identified by spectral analysis in a gas-discharge tube; quant. analysis is carried out with a gas volumetric technique. Full details are given of the methods used, with diagrams of apparatus. Results are tabulated for the amounts of C, Fe, SiO₂, Mg, Cu, Ca, Ti, Pb, Bi, Ag, Ni, Sr, Cr, Ba, Zn, Al, Mn, Na, K, P, Cl, N, SO₂ and O in various grades of sulphur.

S. M. MARSH

467. Investigation of the Wackenroder reaction by means of radiometric paper-chromatographic methods. E. Blasius and W. Burmeister (Tech. Univ., Berlin). *Z. anal. Chem.*, 1959, **168** (1), 1-15.—The course of the Wackenroder reaction has been studied by using reactants labelled with radioactive S and analysing samples, taken from the reaction mixture at intervals, by means of paper chromatography. The paper chromatograms were also evaluated radiometrically to give activity distribution curves. Two series of experiments were carried out with active H₂SO₄ and active H₂S, respectively. The results are detailed and the following mechanism is proposed. Sulphoxylie acid (H₂SO₃) is formed as the primary product, probably by a kind of synproportionation, and this reacts with H₂SO₄ to give trithionic acid, which is in turn saponified by H₂S to give thiosulphuric acid. Thiosulphuric acid reacts with trithionic acid at a given concentration ratio to give tetrathionic acid, which reacts in an analogous way with thiosulphuric acid to give pentathionic acid. Under certain conditions this may be converted into hexathionic acid. Elementary sulphur is formed by the two following reactions—



S. M. MARSH

468. Micro-titration of sulphate ions, with barium rhodizonate as an interface indicator. Eiiti Minami and Kunihiko Watanuki (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *Japan Analyst.*

1959, **8** (3), 175-179.—Barium rhodizonate (I) collects at the interface between water and a mixture of nitrobenzene and *iso*amyl alcohol (1:5, by vol.) and the change in colour is thus observed more clearly (limit of detection for Ba, 3 µg). The red colour of I is stable at pH 2, and a titration of >5 mg of SO₄²⁻ per litre is possible with an error of 4%. There is no interference from Ca, Mg or Al; Fe²⁺ and Pb give coloured compounds with rhodizonate. This method is applicable to water analysis, provided that interfering ions are removed by, e.g., ion exchange. *Procedure*—Adjust the sample soln. (5 to 100 mg per litre) to pH 4 (*p*-nitrophenol) and add BaCl₂ (0.005 M); set aside for 15 min., then add the organic solvent (2 ml) and Na rhodizonate soln. (5 mg per 5 ml, 0.5 ml) and titrate with 0.005 M H₂SO₄, with shaking, until the red colour at the interface is discharged. K. SAITO

469. Colorimetric determination of sulphate ions by means of barium molybdate and thioglycolic acid. Saburo Kanno (Kanagawa Prefectural Public Health Lab., Nakamuri-machi, Minami-ku, Yokohama). *Japan Analyst.*, 1959, **8** (3), 180-185.—Barium molybdate precipitates SO₄²⁻ in a borate buffer of pH ≈ 6 and the liberated MoO₄²⁻ are determined photometrically with thioglycolic acid at 365 mµ. The addition of ethanol reduces the solubility of BaSO₄. The working curve is linear for <25 µg of SO₄²⁻ per ml. The molar extinction coeff. is ten times as great as that for the Ba chloranilate method (cf. Bertolacini and Barney, *Anal. Abstr.*, 1958, **5**, 2185). K. SAITO

470. Polarographic determination of sulphates in Perhydrol. W. Kemula and J. Kornacki (Dept. of Inorg. Chem., Warsaw Univ., Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 831-835.—After a preliminary thermal decomposition, the concn. of SO₄²⁻ is determined indirectly by pptn. with a standard soln. of Pb(NO₃)₂ and the excess of Pb²⁺ is determined polarographically in 50% ethanol soln. Limits for interfering substances are given. H. DMOWSKA

471. Nephelometric determination of sulphates in Perhydrol. W. Kemula, W. Brachaczek and J. Kornacki (Inorg. Chem. Dept., Warsaw Univ.). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 939-948.—The concn. of SO₄²⁻ (3 to 15 µg per ml) is measured in a Pulsfrich nephelometer after treatment of the sample with 0.1 N HCl, 20% of ethanol and solid BaCl₂; Fe²⁺ (0.01%), Al³⁺ (0.02%), Pb²⁺ (0.01%) and PO₄³⁻ (0.05%) do not interfere. When a standard curve is used, the sample should be decomposed before the analysis, but this is not necessary if the method of standard additions is employed. The time occupied is ≈ 2 hr., and the error is > 20% at a concn. of 0.006% of SO₄²⁻. H. DMOWSKA

472. Volumetric method of determination of sulphates in the presence of chromium. R. Kling (Inst. of Inorg. Chem., Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 817-820.—The pH of the sample is adjusted to 4.5 to 5.5 with HCl or NaOH and after the addition of acetone, NH₄Cl and 10% acetic acid the SO₄²⁻ are titrated with BaCl₂, with sodium rhodizonate as external indicator. H. DMOWSKA

473. Chromatographic and polarographic researches on mixtures of higher polythionates. C. Bighi, G. Trabandelli and G. Pancaldi (Ist. Chim. Univ. Ferrara, Italy). *Boll. Sci. Fac. Chim.*

Bologna, 1958, **16** (3), 92-93.—A chromatographic method for the determination of polythionates with S & S. 2043 bM paper and *n*-butanol - acetic acid - H_2O (4:1:5) as solvent is described. Chromatography is continued for 5 hr. R_f values are obtained by ascending and descending techniques. Ammoniacal $AgNO_3$ soln. is used as colour developer. Polythionates with 15 to 20 atoms of S are analysed and the decomposition of higher polythionates during the development is correlated with the disappearance of the spots on the chromatogram. The polarographic measurements on the eluates are compared with the chromatographic observations.

L. ZANONI

474. Colorimetric determination of traces of bromine in selenium for rectifiers. J. Siwecka (Tele- and Radio-tech. Inst., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 1001-1012.—The sample (0.25 to 2.5 g) is dissolved in 50% $NaOH$ soln., oxidised with H_2O_2 , and neutralised to pH 7.4 with H_2SO_4 . The soln. is then brought to pH 1.2 with H_2SO_4 and oxidised with H_2SO_4 in the presence of fuchsin (decolorised with H_2SO_4) and $CHCl_3$. The purple colour of the $CHCl_3$ layer is measured at 574 $m\mu$, and is stable for 72 hr. Beer's law is obeyed over the range 0 to 10 μg of Br per ml, and the method is applicable over the range 0.001 to 0.01% with a sensitivity of 0.0001%.

H. DMOWSKA

475. Separation of tellurium(IV) and selenium(IV) by solvent extraction with tributyl phosphate in kerosine. Mariko Inarida (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (3), 273-275.—Tellurite is quant. extracted from 4 to 12 N HCl with tributyl phosphate in kerosine (one quarter of the vol. of the aq. layer); selenite remains in an aq. phase, < 5 N in HCl. The separation is satisfactory with a single extraction. Tellurite is extracted back into an aq. phase with 0.5 N HCl.

K. SAITO

476. Separation of tellurite ions from sulphate ions by solvent extraction with tributyl phosphate in kerosine. Mariko Inarida (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (3), 280-281.—Since TeO_4^{2-} are quant. extracted from 4 to 12 N HCl with tributyl phosphate in kerosine, a satisfactory separation can be made from a high concn. of SO_4^{2-} , which remain in the aq. phase in the presence of 2 to 12 N HCl. In the presence of both TeO_4^{2-} and TeO_3^{2-} , the TeO_3^{2-} are extracted first, and the TeO_4^{2-} are then reduced to TeO_3^{2-} and similarly extracted.

K. SAITO

477. Determination of tellurium in bismuth metal. F. E. Wild [U.K.A.E.A. (Research Group), C37, Royal Arsenal, Woolwich, London]. A.E.R.E. Report AERE C/R 2666, 1959, 12 pp.—Procedures are described for the determination of Te (5 p.p.m. to 1500 p.p.m. on a 1-g sample). The sample is dissolved in 6 N HCl (10 ml) and HNO_3 (sp. gr. 1.42) (0.5 ml), evaporated to dryness, re-dissolved in HCl (sp. gr. 1.18) (2 ml) and evaporated to dryness. The dissolution in HCl and evaporation are repeated 4 times. The residue is dissolved in HCl (2 ml) and diluted with H_2O (10 ml). Tellurium is ptd. by hydrazine hydrochloride and $SnCl_4$, filtered off in a sintered glass funnel, and re-dissolved in HNO_3 . The determination is completed either volumetrically by titration with $K_2Cr_2O_7$ soln.

(Lenher and Wakefield, *J. Amer. Chem. Soc.*, 1923, **45**, 1423) or absorptionometrically at 420 $m\mu$ (DeMeie, *Anal. Chem.*, 1948, **20**, 488) according to the amount of Te present. T. R. ANDREW

478. Ultra-violet spectrophotometric determination of chromium with the aid of ion-exchange resin. Toru Nozaki and Kaoru Ueno (Fac. of Engng, Ehime Univ., Niihama). *Japan Analyst*, 1959, **8** (3), 185-190.—The extinction at 350 $m\mu$ of Cr^{VI} in < 0.7 N H_2SO_4 is proportional to concn. for < 20 μg per ml. At this wavelength the additive law holds for Fe^{III} , Mn^{VII} , V^{IV} and Ni. By the use of the anion-exchange resin Dowex 1 (60 to 100 mesh), Cr^{III} is separated from Fe^{III} in 10.5 N HCl, but from Mn^{II} only with difficulty (cf. Kraus *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1460). The eluate (containing < 500 μg of Cr) is evaporated to dryness with 25% H_2SO_4 (2 \times 2 ml), diluted to ≈ 15 ml, boiled with 0.01 N $AgNO_3$ (1 ml) and $(NH_4)_2S_2O_8$ soln. (15%) (1 ml) and made up to 25 ml for photometry. In the presence of Mn, the contribution of Mn to the extinction at 350 $m\mu$ is calculated from that at 545 $m\mu$.

K. SAITO

479. Potentiometric determination of free acid in the presence of salts of tervalent chromium. M. T. Serebrennikova and E. I. Tolstikova. *Trudy Ural'sk. Nauch. Khim. Inst.*, 1955, (3), 61-73; *Ref. Zhur. Khim.*, 1959, (9), Abstr. No. 31,052.—Determinations of HCl in the presence of $CrCl_3$, of HNO_3 in $Cr(NO_3)_3$ soln. and acetic acid in Cr acetate soln. were carried out. The test soln. containing \approx 0.02 to 0.3 g of acid and approx. the same amount of chromium salt was made up to 150 ml with H_2O and titrated with 0.1 N NaOH; a pH meter with a glass electrode was used for the end-point detection. Titration curves were plotted for the titration of the pure acids, "combined acids" and salt-acid mixtures. In the titration of free HCl and HNO_3 , the end-points and equivalence-points coincided. In the titration of $CrCl_3$ and $Cr(NO_3)_3$ there was a rapid change in potential from pH 6.5 to 10. In the titration of a mixture of HCl and $CrCl_3$ or of HNO_3 and $Cr(NO_3)_3$ two changes of potential were observed; the amount of free acid was determined by the difference between the titres of the salt-acid mixture and the pure salt. In the titration of Cr acetate there was no sharp potential change; only 13 to 18% hydrolysis occurred, which does not affect the determination of free acetic acid. A curve was plotted of the vol. of NaOH (ml) *vs.* the amount of Cr acetate (g); knowing the amount of Cr in the test soln. the amount of NaOH (ml) required for the titration of Cr acetate can be determined; knowing the vol. of NaOH (ml) required for the titration of the acetic acid-Cr acetate mixture to pH 7, the amount of free acetic acid can be determined by difference. It is suggested that an analogous method could be used for the determination of H_2SO_4 in $Cr_2(SO_4)_3$ soln. K. R. C.

480. Rapid analysis of chromite and chrome ore. J. I. Dinnin (U.S. Geol. Surv., Washington 25, D.C.). *Bull. U.S. Geol. Surv.*, 1959, **1084-B**, 68 pp.—The sample is fused with Na_2O_3 in a zirconium crucible and the major constituents are determined from aliquots of a soln. of the sample prepared by acidifying an aq. extract of the fusion product. Chromic oxide is determined volumetrically by $(NH_4)_2SO_4$ - $FeSO_4$ - $Cr_2O_7^{2-}$ titration; SiO_2 is determined spectrophotometrically by using the reduced molybdate colour; total Fe is determined by a

modified differential spectrophotometric method with 1:10-phenanthroline. An additional aliquot, electrolysed in a mercury cathode apparatus, is used for the titration of MgO with EDTA, and for the spectrophotometric determinations of Al_2O_3 and TiO_2 with alizarin red S and tiron, respectively. The minor constituents are determined on another aliquot from which CrO_3Cl_2 has been volatilised by fuming with HClO_4 and HCl ; MnO , V_2O_5 and NiO are then determined spectrophotometrically by using the permanganate, tungstovanadophosphate, and α -fural dioxime colours, respectively. Separate portions of the sample are used for the determination of CaO , H_2O and FeO . These methods allow a dozen or more samples to be completely analysed in about 5 days, with a precision comparable to that of conventional methods.

R. A. HOWIE

481. Colorimetric determination of molybdenum with phenylthiocarbamide. Sumio Komatsu and Toshio Tadokoro (Fac. of Lit. and Sci., Toyama Univ.). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (1), 47-49.—The use of phenylthiocarbamide (I) in glacial acetic acid was examined for the reduction of molybdenophosphoric acid. The extinction coeff. at $710 \text{ m}\mu$ increases with increase in concn. of the acid and remains constant in the presence of HNO_3 ($>10 \text{ N}$); it also increases with the amount of I, remaining constant in the presence of >10 moles per mole of molybdate. The working curve consists of two straight lines (1 to $8 \mu\text{g}$, and 8 to $12 \mu\text{g}$ of Mo per ml, respectively). Arsenate oxidises I and the permitted concn. is $<1.5 \mu\text{g}$ of As per ml. Coloured cations and V (after reduction with SO_2) are removed with Amberlite IR-120 (Na). Iron is masked with F^- . Ammonium ions do not interfere when the heating is prolonged to 1 hr. An excess of phosphate and of I do not interfere. The error is $<3\%$.

K. SAITO

482. Chromometric determination of molybdenum in the presence of certain elements using platinum and mercury electrodes. A. I. Busev and Gyn Li. *Vestn. Mosk. Univ.*, 1959, (1), 187-195.—Although the titration of Mo^{VI} under the specified conditions is perfectly satisfactory with platinum indicator electrodes, the use of tungsten and graphite indicator electrodes as described previously (cf. Busev and Gyn Li, *Anal. Abstr.*, 1959, **6**, 1285) has several advantages. The conditions for titrating Mo^{VI} with CrCl_3 in an H_2SO_4 medium containing Fe^{III} and Ti^{IV} are studied with platinum and mercury indicator electrodes. Satisfactory results are obtained and the method is recommended for the analysis of certain alloys. The necessity of changing from a platinum to a mercury indicator electrode during the titration is a disadvantage.

K. R. C.

483. Photometric determination of molybdenum in the presence of tungsten as the molybdenum(V)-EDTA complex. E. Lassner and R. Scharf (Metallwerk Plansee A.-G., Reutte/Tirol). *Z. anal. Chem.*, 1959, **168** (1), 30-33.—The yellow colour of the Mo^{V} -EDTA chelate is used for the photometric determination. The almost neutral sample soln. is treated with 10 ml of 10% EDTA soln., 25 ml of 40% tartaric acid soln., 2 to 3 g of hydrazine sulphate and 5 ml of H_2SO_4 (1:1) and boiled for 10 min. Sodium acetate soln. (40%) (10 ml) is then added and, after cooling, the soln. is made up to 250 ml with water. The extinction of the soln. is measured at $446 \text{ m}\mu$ against a reagent blank. The calibration graph is rectilinear and Beer's law holds for the concn. range 2 to 50 mg of Mo per 250 ml of soln.

The relative error is in the range 1 to 3% at concn. of 10 to 50 mg of Mo per 250 ml, and correspondingly higher at lower concn.; it is not increased by the presence of a 500-fold excess of tungsten. Reliable results are obtained even at high concn.

S. M. MARSH

484. Direct spectrographic method of determination of uranium in residues after leaching of ores. Z. Radwan and B. Strzyzewska (Anal. Chem. Dept., Inst. of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 737-744.—Uranium (0.01 to 0.1%) in residues is determined spectrographically in the presence of considerable quantities of SiO_2 , Al, Fe, Ca and Mg. Graphite powder is used as a spectrographic buffer. Results are evaluated by the method of three standards. The line 4241.7 A is used for the total energy method and 4090.1 A for the method of partial evaporation.

H. DMOWSKA

485. Quantitative radiochemical analysis by ion exchange. IV. Uranium and tellurium. L. Wish (Naval Radiological Defense Lab., San Francisco). *U.S. Atomic Energy Comm.*, Rep. USNRDL-TR-312, 1959, 17 pp.—Radiouclides of Te from fission-product mixtures are eluted together with U from Dowex-2 anion-exchange resin in quant. radiochemical procedures. The separation of these two elements from each other is necessary for their determination. The adsorption of Te^{IV} from H_3PO_4 soln. was investigated. From similar data on UVI a procedure for the separation of Te was obtained. Column runs indicated that the yields were quant. and the purities $>99\%$.

NUCL. SCI. ABSTR.

486. Determination of [trace amounts of] uranium in zircon. F. Cuttitta and G. J. Daniels (U.S. Geol. Survey, Washington, D.C., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (5), 430-434.—Concn. of U as low as 0.0005% in zircon can be determined fluorimetrically by fusion and dissolution of the sample (0.1 g), followed by the direct extraction, from 7% (v/v) HNO_3 , of $\text{UO}_2(\text{NO}_3)_3$ with ethyl acetate, Na_2HPO_4 being used to retain the Zr. The extract is evaporated to dryness and the residue is fused with 2 g of a mixture of NaF , Na_2CO_3 and K_2CO_3 (9:45.5:45.5) to obtain the phosphor. After ≈ 30 min. the fluorescence of the button is determined in a reflection fluorimeter (for $>0.01\%$ of U) or a transmission fluorimeter (for $<0.01\%$ of U); the content of U is obtained by reference to phosphor buttons prepared from standard soln. The accuracy is 97 to 98%, and the coeff. of variation is $<2.5\%$ for routine duplicate analyses. The method provides a quant. separation of as little as 0.1 μg of U from 10 mg of Zr.

W. J. BAKER

487. Determination of uranium in uranium dioxide. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 35, 1959, 4 pp.—The method is based on standard analytical practice and is described in detail by J. Walkden.

488. Spectrochemical determination of uranium in silicate minerals rich in other rare elements. S. Held (Israel Atomic Energy Comm.). *Bull. Res. Council Israel*, **A**, 1959, **8** (2), 81-86.—The suitability of various volatile substances to enhance the sensitivity has been studied. When U was determined by the method of single addition in a rock containing allanite, haematite, quartz, felspar and fluorite, and a considerable quantity of Nb,

with GeO_2 as an enhancing agent, the results obtained were in good agreement with those found by chemical analysis.

J. M. JACOBS

489. Separation of uranium from aluminium by cation-exchange resin. Koichi Tonomaki and Makoto Otomo (Fac. of Lit. and Sci., Hiroshima Univ., Amori-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (1), 41-43.—Uranium (<100 mg) is eluted from a column of Amberlite IR-120 (H) (10 mm x 11 cm) with 0.3 to 1 N H_2SO_4 (150 ml) (rate of flow, 2 ml per min.). Aluminium (<9 milli-equiv.) remains on the column, and is then eluted with 2 N HCl (150 ml). The separation is satisfactory in the range of molar ratios of U_3O_8 to Al_2O_3 from 0.01 to 20. K. SAITO

490. Determination of uranium in bismuth-base alloys. U.K.A.E.A. (Res. Group, Woolwich Outstation, Royal Arsenal, London, S.E.18). AERE-AM 27, 1959, 7 pp.—The method is based on reports by H. L. Shallosky (AERE C/R 1869) and F. E. Wild (AERE C/R 1868).

491. Separation of uranium from accompanying metals by the carbonate method. L. Wodkiewicz (Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 789-792.—After reduction of Cr^{4+} and Mn^{4+} to Cr^{3+} and Mn^{3+} with ethanol, interfering elements are removed from an acid soln. of the ore by Na_2CO_3 and FeCl_3 . Uranium (0.01 to 1.0%) is determined colorimetrically in the filtrate. Errors range from -4 to +7%. The time required for the separation is one-third of that needed in previous methods. H. DMOWSKA

492. Method for the determination of hydrogen in uranium. J. T. Waber and E. S. Wright (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. AECD-4280, [1955?], Decl. Jan., 1956, 9 pp.—The hydrogen is extracted from the hot uranium metal by pumping. The sample is held in a vacuum (approx. 10^{-8} torr) before heating to 500°. The gas which is evolved at this temp. is transferred by an automatic Toepler pump into a small vessel of known volume and the pressure is read with a precision cathetometer. A small virtual leak in the vacuum system contributes a blank, which is proportional to the duration of the extraction. The content of H is computed by the ideal gas law from the known pressure, temp. and vol. NUCL. SCI. ABSTR.

493. Spectrographic determination of impurities in pure uranium. I. Determination of boron, iron, manganese, magnesium and aluminium. Tokunosuke Nakajima, Masao Takahashi and Hiroshi Kawaguchi (Japan Atomic Energy Res. Inst., Tokai, Ibaragi-ken). *J. Japan Inst. Metals, Sendai*, 1958, **22** (10), 508-512.—Scribner's method of arc excitation for impurities in uranium in the presence of Ga_2O_3 (*J. Res. Nat. Bur. Stand.*, 1946, **37**, 379) was examined with reference to the loss of impurities, especially of B, during the conversion of U into U_3O_8 by heating. The extent to which B is lost increases with increase in its concn. The heat treatment (800°, 1 to 4 hr.) must be carefully controlled for both samples and standards. The conditions for arc excitation are—d.c. 10 amp.; exposure, 30 sec.; arc gap, 4 mm. The line pairs employed are those used by Scribner.

II. Determination of rare-earth elements. Tokunosuke Nakajima, Masao Takahashi and Hiroshi Kawaguchi. *Ibid.*, 1958, **22** (11), 564-568.—The concn. of rare-earth elements (>0.1 p.p.m.) (Short

and Dutton, *Anal. Chem.*, 1948, **20**, 1073; Hirt and Nachtrieb, *Ibid.*, 1948, **20**, 1077) in uranium was examined with radioactive ^{149}Eu and ^{144}Eu . Extraction of rare-earth elements from $\text{UO}_3(\text{NO}_3)_6$ (20 g of U_3O_8) in diethyl ether (80 ml) is best effected with 4 N HNO_3 . The amount of U in the aq. layer is <2 g. The rare-earth elements are pptd. with HF (48%) (18 ml) within 12 hr., together with La (1 mg). The fluorides are treated with H_2SO_4 (1 ml), dissolved in HCl (6 N) (3 ml) and pptd. with aq. NH_3 in the presence of salicylic acid (0.05 g). The product is dissolved in 3% HCl (1 ml) containing 10 μg of Cr as internal standard, and one drop (0.05 ml) is placed on a copper electrode (diam. 8 mm) for spectrographic analysis by the method of Fred et al. (*J. Opt. Soc. Amer.*, 1947, **37**, 279).

K. SAITO

494. Separation of the major impurities in uranium dioxide prior to spectrographic examination. U.K.A.E.A. (Res. Group, Chem. Div., H.M. Gun Wharf, Chatham, Kent). AERE-AM 34, 1959, 3 pp.—The method is based on that of Burstall and Wells (*Analyst*, 1951, **76**, 396) and Wild (A.E.R.E. Report C/R 1868). It is written with full details by J. Walkden and K. E. Heathfield.

495. Spectrographic determination of impurities in uranium oxide by means of carrier distillation. J. Czakow, L. Pszonicki and Z. Walewska (Anal. Chem. Dept., Inst. of Nuclear Res., Polish Acad. of Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 753-760.—The method of Scribner and Mullins (*J. Res. Nat. Bur. Stand.*, 1946, **37**, 379), with modifications, is adapted for the spectrographic determination of impurities in U_3O_8 by distillation in a d.c. arc. H. DMOWSKA

496. Determination of silicon in uranium dioxide. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 37, 1959, 4 pp.—The method is based on standard analytical procedure and is written with full details by J. Walkden and K. E. Heathfield.

497. Determination of vanadium in uranium dioxide. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 38, 1959, 3 pp.—The method is adapted from that of P. H. Scholes (*Analyst*, 1957, **82**, 525) and is described in detail by J. Walkden.

498. Spectrometric determination of impurities in nuclear-pure uranyl nitrate. T. Nowicka-Jankowska, A. Gotkowska, I. Pietrzak and W. Zmijewska (Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 977-1000.—Methods are described for the following determinations over the concn. ranges and with the relative mean errors stated:—Ni (1 to 10 p.p.m.) with dimethylglyoxime ($\pm 10\%$); Al (1 to 20 p.p.m.) with haematoxylin ($\pm 10\%$ for <5 p.p.m., $\pm 5\%$ for >5 p.p.m.); Si (>5 p.p.m.) by the molybdenum blue method ($<\pm 10\%$); Mo (1 to 5 p.p.m.) with thiocyanate ($<\pm 10\%$), (1 to 10 p.p.m.) with toluene-3:4-dithiol ($<\pm 10\%$); Cr (1 to 10 p.p.m.) with sym-diphenylcarbazide ($<\pm 10\%$); and Fe (1 to 5 p.p.m.) with 2:2'-dipyridyl ($<\pm 10\%$). H. DMOWSKA

499. Separation of metals by ion-exchange resins. III. Separation of UXI from uranyl nitrate by the nitrate elution method. Ying-Mao Chen (National Taiwan Univ., Taiwan, China). *J. Chinese Chem. Soc., Taiwan*, 1957, [2] **4**, 47-55 (in English).—When 40 g of uranyl nitrate in 7.5 N HNO_3 (I) was

passed through a column of 10 g of dry Amberlite IRA-400 (nitrate form), the UX_1 was retained on the resin; uranyl ions adsorbed were eluted with I until the washings did not give a positive reaction with $K_4Fe(CN)_6$. The UX_1 retained on the resin was recovered by eluting with water. The eluate (A) was collected in 5-ml fractions, each of which was evaporated to dryness. The activity of the residue was measured with a Geiger-Müller counter through an aluminium absorber (20.5 mg per sq. cm), by which the weak β -radiation of UX_1 was eliminated and only the 2.3-meV β -radiation of UX_2 (1.1-min. daughter of UX_1) was counted. The decay curves were made for 100 hr. In the batch method, the highly active fractions of eluate A were used. After adding 1 mg of Th as a carrier and neutralising, filtering, and washing, the ppt. was dissolved in the minimum amount of $HClO_4$, and diluted to 100 ml. A mixture of 1 ml of this soln. with 0.5 g of Amberlite IRA-400 (nitrate form), conc. HNO_3 and water (to make 10 ml with a concn. of HNO_3 of 7.5 N) was set aside for 1 day, then two 2-ml samples were taken and their activities determined. The effects of the presence of anions on the distribution of UX_1 in the Amberlite resin were examined with the batch method by adding 0.01 to 0.05 M Na_2SO_4 , $(NH_4)_2HPO_4$, $KBrO_3$, KIO_3 , KCl , KBr , KI and Na oxalate. The activity adsorbed was calculated from the difference of the total activities and that present in the soln. Except for phosphate and iodate (both are sparingly sol. in acid soln. and reduced the adsorption to some extent), none of the anions studied had any appreciable effect on the adsorption. The calculation of the distribution coeff. for UX_1 at various concn. of HNO_3 with the Tompkins and Mayer's equation showed that, the greater the concn. of HNO_3 , the more UX_1 will be adsorbed from eluate A. At concn. of HNO_3 > 7.5 N, the adsorption of the UX_1 decreases with increase in the concn. of the HNO_3 . This is also true for the column method. The more concentrated the washing acid the greater is the yield of UX_1 , and this is > 85% when concn. of HNO_3 > 7 N are used, both in the column and the batch methods.

CHEM. ABSTR.

500. Determination of submicrogram quantities of plutonium-239. G. J. Hunter and R. B. Chenley [U.K.A.E.A. (Res. Group), C.37, Royal Arsenal, Woolwich, England]. A.E.R.E. Analytical Method AERE-AM 19, 1959, 7 pp.—The Pu as PuF_3 or PuF_4 is co-precip. with LaF_3 ($\approx 500 \mu\text{g}$ of La) from a soln. containing acetate at pH 3.3. After being thoroughly washed, the ppt. is mounted on a stainless-steel disc and α -counted. Up to 1 g of U can be tolerated. Details are given of the calculations involved in the method. The effect of the no. of counts on the coeff. of variation, which can be as low as 2%, is considered. [Cf. Chenley *et al.*, *Anal. Abstr.*, 1959, **6**, 544.]

G. J. HUNTER

501. Separation of neptunium and plutonium by ion exchange. N. Jackson and J. F. Short (Chem. Div., A.E.R.E., Harwell, England). AERE-M 444, 1959, 6 pp.—Neptunium-237 ($4.5 \times 10^4 \alpha$ c.p.m.) and ^{239}Pu ($1.5 \times 10^6 \alpha$ c.p.m.), after dissolution and reduction to Np^{IV} and Pu^{III} in a saturated soln. of NaI in conc. HCl (1.5 ml), can be separated completely by passing the soln. through an ion-exchange column (8 cm \times 2 mm, De-Acidite FF, column vol. 4 drops) at a rate of two drops per min. The percolate containing Pu, plus a wash of three

column-volumes is collected on a watch-glass, evaporated to dryness and counted. The ^{237}Np is then eluted from the column with 2 M HCl , not less than eight column-volumes being used. The yield is 100% for each element. With a larger column (20 cm \times 2.5 cm) and a flow rate of 1 ml per min., ≈ 2 to 3 g of ^{237}Np can be purified from 50 mg of ^{239}Pu .

W. J. BAKER

502. Analytical method for neptunium-237 using anion exchange. F. P. Roberts (Gen. Electric Co., Hanford Atomic Products Operation, Richland, Wash.). U.S. Atomic Energy Comm., Rep. HW-59032, 1959, 14 pp.—A method was developed for the separation of Np from Pu, U, Am, Cm and fission products by anion exchange, with sufficient decontamination to permit of the determination of ^{237}Np by α -energy analysis and that of ^{239}Np by γ -spectrometry. The sample is spiked with ^{239}Np tracer so that yield corrections may be made, and adsorbed on a small column of Dowex 1X-4 (100 to 200 mesh) from 8 N HNO_3 in the presence of ferrous sulphamate and semicarbazide. After washing the resin with 30 to 40 column-volumes of 4.5 N HNO_3 containing ferrous sulphamate and semicarbazide, the Np is eluted with 0.005 M $Ce(SO_4)_2$ in dilute HNO_3 and mounted for total α -counting, α -energy analysis and γ -energy analysis. Recoveries of Np of 95% have been obtained, while Pu decontamination factors are 5×10^4 . Decontamination factors for U, Am, Cm and gross fission products are all $> 10^4$. Uranium (< 180 g per litre) in the column feed does not interfere. The Pu decontamination factor can be increased by a factor of 10 to 100 by following the HNO_3 -ferrous sulphamate- semicarbazide wash by a wash with 0.1 M NH_4I in 12 N HCl. This is followed by elution of Np with 6.5 N HCl containing 0.004 N HF. The method is applicable to the high-salt samples from the Redox process as well as to Purex process samples.

NUCL. SCI. ABSTR.

503. Polarographic determination of fluorides. J. Volf and J. Havránek. *Pracovní Lékařství*, 1958, **10** (3), 253-256.—The complex of Al with 1-(2-hydroxy-5-sulphophenylazo)-2-naphthol, and the reagent alone, yield well-developed polarographic waves, the heights of which change in the presence of F^- (in acetate buffer soln. of pH 4.63), as Al forms a complex with F^- and an equiv. amount of the reagent is thus liberated. Amounts of 1 to 50 μg of F^- in 10 ml can be determined with an error of $\pm 7\%$.

J. ZVÍKA

504. Potentiometric determination of active chlorine, chlorides and chlorates in chlorinated lime. J. Galius-Olender (Inst. Inorg. Chem., Gliwice, Poland). *Chem. Anal.*, Warsaw, 1958, **3** (5-6), 859-863.—A platinum - calomel electrode pair is used in the potentiometric determination of active chlorine, chlorides and chlorates; 0.1 N As_2O_3 is used as titrant in the chlorine determination and 0.1 N $AgNO_3$ for chloride. For chlorates, an excess of $FeSO_4$ is added after the titration with As_2O_3 , and this is back-titrated with $KMnO_4$.

H. DMOWSKA

505. Determination of chloride ion concentration by argentipotentiometry. E. Naumann (Inst. f. Tech. Chem., Univ., Jena). *Angew. Chem.*, 1959, **71** (9), 309-310.—The concn. of Ag^+ may be determined by the potential of a silver electrode immersed in the soln. By adding a suspension of $AgCl$ to a soln. containing Cl^- and measuring the

potential of the silver electrode it is possible to calculate the initial Cl^- concn. This method has been applied to soln. of 0.01 N down to $10^{-4} N$ in Cl^- .

T. R. ANDREW

506. Determination of chlorine in beryllium, thorium or uranium metals or their oxides. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 42, 1959, 6 pp.—The sample is heated to 1100° to 1200° in a current of steam. The HCl formed is collected in the condensate and the Cl determined absorptiometrically after the addition of mercuric thiocyanate and $(\text{NH}_4)_2\text{SO}_4\text{Fe}_2(\text{SO}_4)_3$. The pyrohydrolysis procedure is based on that of C. J. Rodden ("Analytical Chemistry of the Manhattan Project," pp. 729-731, McGraw-Hill Book Co., New York, 1960), and the Cl determination on that of J. S. Swain [Chem. & Ind., 1956, (20), 418] and Bergmann and Sanik [Anal. Abstr., 1957, 4, 2670]. The method has been written with full details by J. Walkden.

G. S. ROBERTS

507. Rapid estimation of chlorate in presence of perchlorate. B. K. Sadananda Rao and G. S. Laddha (Univ. of Madras, India). Z. anal. Chem., 1959, 107 (6), 410-415 (in English).—Quinoline yellow (C.I. Acid Yellow 3) is used as indicator in the titration of an acid soln. (H_2SO_4 or HCl) of the mixture with TiCl_3 in the presence of NaBr. With experience, an accuracy within 1% can be attained.

E. G. CUMMINS

508. Polarographic determination of iodine in aqueous solutions. Z. Przybylski (Geochem. Lab., Petroleum Inst., Kraków, Poland). Chem. Anal., Warsaw, 1958, 3 (5-6), 849-857.—Iodides are oxidised to iodates by 0.2 N NaBrO in 0.5 N NaOH containing a little NaBrO_3 , and then determined polarographically in the presence of Na_2SO_3 . The influence of other cations and anions is discussed. The iodine (0.2 to 120 mg per litre) is determined with a mean error within 2%, and results for petroleum brines agree with those by older methods to within $\pm 5\%$.

H. DMOWSKA

509. Iodate method for the determination of iodides, with phenazone to absorb iodine. E. Schulek and K. Burger (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). Pharm. Zentralh., 1959, 98 (5), 242-244.—The absorption of iodine by phenazone (I) in this determination enables starch to be used as indicator and over a wider pH range; the need for determining I^+ with KCN is also avoided. The accuracy on 1.7 to 11.3 mg of KI is within $\pm 0.2\%$. A 10-fold excess of Cl^- does not interfere, but the concn. of Br^- must be $> 10\%$ of that of I^- . In the presence of 10% of Br^- , the max. permissible Cl^- content is 60% of that of the I^- . Procedure—Dissolve the iodide (2 to 10 mg) in 20 ml of H_2O and add 50% H_2SO_4 (10 ml). Dissolve 0.5 g of I in this mixture and titrate with 0.01 N $\text{KH}(\text{IO}_6)_2$, with 1% starch soln. (1 to 2 ml) as indicator. Near the end-point add successive drops at 5 to 10-sec. intervals until the blue colour is discharged.

J. P. STERN

510. Polarographic determination of iodides in fused salts. R. M. Novik and Yu. S. Lyalikov (Kishinev State Univ., U.S.S.R.). Zhur. Anal. Khim., 1958, 13 (6), 691-694.—In the polarographic determination of I^- at 270° to 360° in molten nitrates as supporting electrolyte two distinct waves are obtained. The first (oxidation potential *vs.* the platinum electrode = $+0.8$ to $+0.6$ V) corresponds

to the anodic oxidation of I^- . The second or NO_3^- wave is absent when NO_3^- are present, and develops only on the addition of I^- ; on acidifying with KHSO_4 this wave disappears, but the first is unaffected. The addition of NaNO_3 augments the height of the second wave. The formation of NO_3^- after the addition of KI is explained by the following reaction—



Potentiometric investigation confirms this reaction. The polarographic determination of I^- is possible in spite of this reaction. At $340^\circ \pm 5^\circ$, $E_f = 0.32 \pm 0.02$ V and is very nearly proportional to the concn. of I^- . The polarographic determination of I^- at 700° to 750° can also be carried out with molten chlorides as supporting electrolyte and the amperometric titration of I^- is possible with AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$.

W. ROUNO

511. Coulometric titration with electrogenerated tin(II). Determination of iodine, bromine and various oxidants via iodometry. A. J. Bard and J. J. Lingane (Harvard Univ., Cambridge, Mass., U.S.A.). Anal. Chim. Acta, 1959, 20 (5), 463-471.—Procedures are given for the following coulometric titrations with Sn^{4+} generated electrolytically (with $\approx 100\%$ efficiency) at a gold or platinum cathode, a.c.d. from 10 to 80 mA per sq. cm, and a supporting electrolyte of 3 to 4 M NaBr plus 0.2 N HCl plus 0.2 M SnCl_4 —(i) of Br or I (the max. error is $\approx \pm 0.3\%$), (ii) of iodate, Fe^{3+} or Ce^{4+} , each iodometrically (the max. error is $\approx \pm 0.5\%$), and (iii) of p -benzoquinone or quinol by direct and reverse titrations (the mean error is $\approx \pm 0.2\%$). The formal potential of the Sn^{4+} - Sn^{2+} couple in acidic bromide medium is $+0.27$ V *vs.* the S.C.E. For iodometric determinations the soln. is first deaerated and then made 0.01 M in KI before adding the sample of the oxidant. Nitrogen is passed over only the surface of the soln. during titration; end-points can be determined potentiometrically or amperometrically. In the titration of p -benzoquinone, an excess of Sn^{4+} is generated and then the excess is back-titrated with Br (generated at a platinum anode); in titrating quinol, Br is generated slightly in excess of the end-point and is then back-titrated with Sn^{4+} .

W. J. BAKER

512. Volumetric determination of manganese after oxidation to the tervalent state. I. G. Ryss and B. S. Vitukhovskaya (Dnepropetrovsk Inst. Rail. Engineers, USSR). Zhur. Anal. Khim., 1959, 14 (3), 318-321.—Since Mn^{4+} are oxidised quant. to fluoromanganese when heated with NH_4NO_3 and HF and fluoromanganese can be determined iodometrically or by titration with $(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ soln. in the presence of diphenylamine the method may be used for determining Mn^{3+} ; Fe^{3+} , Cr^{3+} , Co^{2+} and Ni^{2+} do not prevent oxidation of Mn^{3+} . Owing to the slow rate of reduction of the sparingly soluble $\text{Cr}^{3+}\text{MnF}_6\cdot 6\text{H}_2\text{O}$ by iodide, boric acid and HCl must be added. When Cr and Fe are present at the same time, the soln. must be titrated with $(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4\cdot 6\text{H}_2\text{O}$. The method was tested by an analysis of ferromanganese containing 74.9% of Mn; a sample (0.5 g of Mn) was dissolved by heating with 49% HNO_3 (15 ml); an equiv. amount of NH_4F was then added and heating continued for 10 min., followed by the addition of 30% HNO_3 (50 ml) and dilution with H_2O to a vol. of ≈ 200 ml. The mixture was titrated with $(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ soln. in the presence of diphenylamine with highly satisfactory results.

K. R. C.

513. Reductometric method for the determination of manganese. A. Kainzner and F. Neudorfer, *Zement-Kalk-Gips*, 1958, **11**, 294-296.—The complexometric method of Přibil and Horáček for the determination of Mn by the addition of EDTA (disodium salt) (I) followed by potentiometric titration (*Brit. Abstr. C*, 1950, 442) is modified for visual titration with FeSO_4 soln. in the analysis of cements, slags and silicates. To a sample (0.5 to 1.0 g) add water (20 to 30 ml) and boil with HCl to drive off H_2S . Add a few drops of H_2O_2 and evaporate to dryness. Take up the residue with water and HCl and filter. Dilute the filtrate to 150 ml with cold water so that the temp. is $<20^\circ$, bring the pH to 4.0 to 4.5 with solid Na acetate, and buffer with a soln. of acetic acid - Na acetate to pH 3.8 to 4.3. Add a mixture of I and PbO_2 (4:1) (1 to 2 g) and stir for 1 to 2 min. Filter the pink soln. through glass wool and titrate with standard FeSO_4 soln. In the presence of $>1.5\%$ of Fe add aq. NH_3 or Na_2CO_3 to the original HCl soln. of the sample to incipient pptn. of R_2O_4 , dilute to 200 ml and add solid Na acetate to complete the pptn. of R_2O_4 and silicates. Cool the filtrate to $<20^\circ$, add the buffer soln. and the I - PbO_2 mixture, and filter and titrate as described above.

CHEM. ABSTR.

514. Analytical use of 8-mercaptoquinoline (thioxine) and its derivatives. IV. Photometric determination of small amounts of manganese. Yu. A. Bankovskii, A. F. Ievin'sh and E. A. Luksha (Inst. Chem. Acad. Sci., Riga, Latvia). *Zhur. Anal. Khim.*, 1959, **14** (2), 222-226.—At pH ≈ 10 , thioxine (I) forms a stable complex with Mn, which is insol. in H_2O and aliphatic hydrocarbons, very slightly sol. in CS_2 and CCl_4 and sol. in most organic solvents to give an intense-brown soln. Its soln. in chlorobenzene, benzene, toluene and xylene are stable for two days. *Procedure*—To the slightly acid test soln. (15 to 20 ml) add 5% ascorbic acid soln. (2 ml), 5% NaOH soln. dropwise to pH 7 to 8, and 6% KCN soln. (5 ml); heat to boiling, cool and add borate buffer soln. to make up to 50 ml and to raise the pH to ≈ 10 . Add a soln. of I in CCl_4 (1 ml), shake vigorously, then add pure CCl_4 (9 ml) and shake again. Separate the organic phase and repeat the extraction. To the combined extracts add dil. HCl (25 to 30 ml) to bring the pH to 3 and shake vigorously; Mn passes into the aq. phase. Wash the aq. phase with CCl_4 (2×5 ml). Repeat the whole procedure on the aq. phase from the addition of ascorbic acid to the addition of CCl_4 , using the same quantities. Separate the organic extract, filter it through cotton wool and determine the extinction at 413 m μ ; refer the results to a calibration curve. Alkali and alkaline-earth metals, Al, Cr, Zr, Th, Ti, La, Au and Ag do not interfere; Fe, Ni, Co, Pd and some other elements are masked by the KCN; ≈ 20 mg of Pt interferes; Pd, Ir and Os do not interfere in milligram amounts; Pb, Zn, Cd, Tl, V and Sn must be absent.

K. R. C.

515. Determination of manganese in beryllium compounds (fluoride, hydroxide and fluoroberyllium). U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 52, 1959, 3 pp.—The method is based on standard analytical practice and is described in detail by J. Walkden.

516. Detection of rhenium with diphenylcarbazide. N. Ghosh (Univ. Coll. Sci., Calcutta). *Sci. & Cult.*, 1958, **23**, 657.—Rhenium in its highest valency

state reacts with diphenylcarbazide (I) in HCl and ethanol to give an intense violet colour with extinction max. at 548 and 440 m μ . Dilute a 0.5-ml aliquot of an aq. soln. containing 0.01% of potassium perrhenate to 25 ml with 0.05% I in HCl (sp. gr. 1.18) and ethyl acetate (2:3, v/v). The colour develops in 30 min.

CHEM. ABSTR.

517. Detection and determination of rhenium. A. I. Lazarev (Akmolinsk Agric. Inst., USSR). *Zhur. Anal. Khim.*, 1959, **14** (3), 362-364.—Calcium perrhenate gives a coloured compound with Sn^{4+} and SO_4^{2-} in the presence of HCl. The max. absorption of the Re complex occurs in the u.v. region; the mol. coeff. of absorption is 1.1×10^4 . Beer's law is obeyed at concn. up to $\approx 8 \mu\text{g}$ of Re per ml. The relative error for the determination of Re is $>7\%$; up to 0.2 mg of V in the soln. does not interfere and NO_3^- up to 0.1 M do not interfere; Ni, Cr, Co, Mo and W interfere. The coloured Re complex can be extracted with butanol or isooctyl alcohol and is stable in the alcohol layer for one hour. For the detection of Re add conc. HCl (2 ml) to the test soln. (2 ml), stir, add M Na₂SO₄ (0.25 ml) and 5% SnCl₄ (0.25 ml) dissolved in conc. HCl. The colour takes 3 to 5 min. to develop. The method can be used to detect 0.5 μg of Re.

K. R. C.

518. Study of the rhenium reaction with methyl violet. I. Extraction of the methyl violet complex of rhenium. A. T. Pilipenko and A. T. Obolonschik. *Ukr. Khim. Zhur.*, 1958, **24** (4), 506-509; *Ref. Zhur. Khim.*, 1959, (7), Abstr. No. 23,058.—The perrhenate complex of Re with methyl violet (I) can be extracted with aromatic hydrocarbons (benzene, toluene, xylene) over a wide range of pH; the best extractant is toluene. The optimum pH range for the extraction of the perrhenate complex with I is 3.5 to 5; at pH <3.5 , the complex is not formed quant. and at pH >7.3 I is decomposed. A soln. of the complex in toluene has a max. extinction at 330 m μ ($\epsilon = 229,500$), at 540 m μ ($\epsilon = 28,000$) and at 600 m μ ($\epsilon = 39,500$). For the detection of Re, a large excess (≈ 45 to 50-fold) of I must be added, owing to the instability of the Re - I complex. The sensitivity of the reaction to pure salts is 0.1 μg of Re per ml; the reaction is highly specific. The determination of Re is not affected by the presence of a 40-fold excess of Mo, but when the Mo to Re ratios are large a partial formation of mixed crystals of complexes of Re and Mo with I occurs. The colour of the soln. of the Re - I complex in toluene is proportional to the concn. of Re and can be utilised for the photometric determination of Re.

K. R. C.

519. New method for separating rhenium and molybdenum. V. M. Tarayan and L. G. Mushegyan. *Dokl. Akad. Nauk Arm. SSR*, 1958, **27** (3), 157-160; *Ref. Zhur. Khim.*, 1959, (10), Abstr. No. 34,574.—It is shown that, in H_2SO_4 soln., salts of Hg^{2+} reduce Mo to the quinquevalent state; ReO_4^{4-} are not reduced. Thus Hg^{2+} may be used as a selective reducing agent in the extraction of Mo, before determining Re by the thiocyanate method. To the test soln. containing 1 to 50 μg of Re and 0.2 to 1.0 mg of Mo add H_2SO_4 to a concn. of 2 N, add KSCN and 3 or 5 drops of 0.1 N $\text{Hg}(\text{NO}_3)_2$, and extract with diethyl ether ($\times 2$ or 3). Add 8 to 10 ml of HCl to the aq. layer, add SnCl₄ and set aside for 10 min.; extract the thiocyanate complex of Re with *n*-butanol and measure the extinction of the extract at 428 m μ .

C. D. KOPKIN

520. Colorimetric determination of rhenium in molybdenum concentrates. A. N. Grunina and A. D. Ulezko. *Sb. Nauch. Trud. Irkutsk. Nauch.-Issled. Inst. Redk. Met.*, 1958, (7), 29-31; *Ref. Zhur. Khim.*, 1959, (9), Abstr. No. 31,017.—To 1 g of finely ground molybdenum concentrate add 0.1 g of KMnO_4 and 3 g of CaO , mix, cover with a layer of 3 g of CaO and ignite at 650° to 700° for 2 hr. Cool, transfer the residue to a beaker, add cold water (100 ml), stir for 30 min. and filter off the CaMoO_4 . Wash the ppt. on the filter with cold water, evaporate the filtrate to 25 or 30 ml, filter off the resulting ppt. and wash it with hot water. To the filtrate add conc. HCl (25% of the vol. of filtrate), and transfer the soln. to a separating-funnel containing 25 g of mercury; add 2 ml of a 20% soln. of KSCN and 2 ml of a 35% soln. of SnCl_4 (35 g of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 20 ml of 50% HCl and made up to 100 ml), mix, set aside for 5 or 7 min. to reduce Re^{VII} to Re^{VI} , add 5 ml of diethyl ether and extract the thiocyanate complex of Re^{VI} . When the sample contains $>0.002\%$ of Re the extraction is repeated. Combine the ether extracts and estimate the colour visually, with a standard soln. of Re for comparison. The error is $\approx 10\%$ for 0.002 to 0.003% of Re .

C. D. KOPKIN

521. Volumetric method for the micro-determination of iron with decinormal potassium permanganate solution. S. Görög and M. Beck (Inst. of Inorg. and Anal. Chem., Sci. Univ. of Szeged, Hungary). *Magyar Kém. Foly.*, 1959, 85 (5), 201-204.—The method is based on the catalytic effect of the complex of triethylenetetramine (**I**) and Fe^{2+} on the decomposition of H_2O_2 . *Procedure*—Adjust the pH of the test soln. to pH 2 to 2.5 with conc. HNO_3 followed by boiling, or use NaHCO_3 . On another sample determine the vol. of 0.1 N NaOH needed to raise the pH to 10. Into a 100-ml beaker, pour sufficient H_2O_2 to bring the final vol. to 10 ml, followed rapidly and in this order, away from direct sunlight, by the unknown (e.g., 2 ml), 2 ml of a soln. of the HNO_3 derivative of **I** (containing 1.702 g of **I**.2 HNO_3 in 250 ml of soln., prepared by the method of Jonassen *et al.*, *J. Amer. Chem. Soc.*, 1950, 72, 2430), the required vol. of 0.1 N NaOH , and 0.5 M H_2O_2 (2 ml, standardised against 0.1 N KMnO_4). Exactly 3 min. after the addition of the H_2O_2 , add 2 M H_2SO_4 (10 ml) and back-titrate the excess of H_2O_2 with KMnO_4 soln. Take the mean of several determinations; if 75% of the H_2O_2 is used up (i.e., $>1.2 \mu\text{g}$ of Fe^{2+} is present), repeat with a more dil. soln. By replacing the unknown with 1.5×10^{-3} M $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ (0 to 2 ml), at a temp. within $\pm 2^\circ$ of the previous determinations, carry out several parallel determinations so as to obtain a calibration curve based on 6 to 8 points. Plot the percentage of H_2O_2 used against the concn. of Fe^{2+} . When carrying out a blank with pure compounds and the same apparatus, $\approx 5\%$ of the H_2O_2 is used up; this corresponds to 0.03 μg of Fe , and is the smallest amount that can be determined. The error of the mean of 4 to 5 determinations is $<3\%$. Complex-forming anions (e.g., EDTA) interfere; others (e.g., Cl^- , F^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) do not interfere even at a concn. of 10^{-3} M. Transition metals that form a complex with **I** interfere at a concn. of 10^{-3} M; Mn^{2+} interfere even at 10^{-6} M. Alkali- or alkaline-earth salts can be present in 10^3 -fold molar concn. with respect to Fe^{2+} ; with other metal salts, the permissible proportion is 10^4 .

A. G. PETO

522. Extraction of ferric iron from chloride solutions with tribenzylamine in chloroform. A. M.

Dýmov and V. V. Koreneva. *Nauch. Dokl. Výssh. Shkóly Metallurgiya*, 1958, (3), 269-272; *Ref. Zhur. Khim.*, 1959, (9), Abstr. No. 31,018.—The extraction of Fe^{3+} from chloride soln. with tribenzylamine (**I**) in CHCl_3 is studied as a function of the concn. of HCl , the duration and number of the successive extractions, the ratio of the volumes of the organic and aq. phases, and the concn. of Fe . Complete extraction of Fe (>40 mg per ml) is achieved from <8 N HCl containing $<8\%$ of **I** and is 100% in one extraction with a 1:1 ratio of organic and aq. phases. The equilibrium between the two phases is established in 2 or 3 min. On decreasing the concn. of HCl below 8 N the extraction of the Fe falls considerably. With concn. of Fe >40 mg per ml, a second extraction ensures the effective recovery of the Fe .

C. D. KOPKIN

523. Accurate determination of iron in oxides. I. Comparison and selection of methods. L. Balabanoff K. (Lab. de Metalurgia, Univ. Concepción). *Bol. Sci. Chil. Quim.*, 1958, 8 (1-2), 12-18.—Methods available for the determination of total, ferric and ferrous iron in small samples (10 to 50 mg) are critically reviewed. The method preferred is based on reduction with stannous chloride, removal of the excess of reductant with HgCl_2 and subsequent titration with $\text{Ce}(\text{SO}_4)_2$ soln., with diphenylaminosulphonic acid as indicator. Full working details are given for the attainment of the highest precision ($\pm 0.05\%$).

E. C. APLING

524. Concentration of traces of iron from solutions of nickel, cobalt and zinc salts by partial precipitation of the macro-component. V. I. Lotareva and V. T. Chukko. *Trudy Leningr. Tekhnol. Inst. im. Lensovetza*, 1958, (48), 119-123; *Ref. Zhur. Khim.*, 1959, (11), Abstr. No. 38,322.—It is established that the degree of concentration of Fe in the ppt. on partial pptn. of Ni or Co as the basic salt is determined by the amount of Ni or Co pptd., the period of contact of the ppt. with the soln. and the dilution of the soln., but is independent of the concn. of Fe . Quantitative concentration of the Fe in the ppt. is attained by pptg. approx. 2.2% of the amount of Ni or Co from dil. soln. (≈ 0.3 M). It is suggested that Fe is taken up by the basic salts of Ni or Co as a result of ion exchange. The exchange is irreversible, so that it may be assumed that the process is complicated by side effects.

C. D. KOPKIN

525. Examination of various methods for the determination of iron, manganese and zinc in ferrites. Hiroshi Kitagawa and Yoshito Aimoto (Hitachi Central Res. Lab., Kokubunji, Tokyo). *J. Japan Inst. Metals*, Sendai, 1958, 22 (8), 389-393.—The titration of Fe^{2+} with KMnO_4 after reduction with zinc amalgam in 3 to 4 N H_2SO_4 gives high results, presumably owing to the formation of Mn^{2+} . The photochemical reduction of Fe in the presence of oxalate (cf. Sastri and Sarma, *Anal. Abstr.*, 1956, 3, 2090) yields satisfactory results with H_2VO_4 (prepared from V_2O_5 and 3 N H_2SO_4) as titrant. Reduction with SnCl_2 is also satisfactory when followed by titration with H_2VO_4 in the presence of oxalic acid and diphenylamine, or with $\text{Ce}(\text{SO}_4)_2$ in the presence of ferroin. An EDTA titration of Fe , Mn and Zn in ferrite was developed by a modification of the method of Flaschka and Pischel (cf. *Anal. Abstr.*, 1956, 3, 2012). *Procedure*—Dissolve the sample (0.5 g) in HCl (1:1) (30 ml), dilute to 100 ml and neutralise a 20-ml aliquot with aq. NH_3 (1:4). Acidify with HCl (1:2) and

add Na acetate soln. (10%) until the soln. becomes red; adjust to pH 1.5 to 2, with HCl, and dilute to 180 ml; add sodium azide (0.1 g) and Naphthol green B (C.I. Acid Green 1) (0.1%) (5 ml) and titrate the Fe with EDTA (disodium salt) soln. Make another 20 to 40-ml aliquot alkaline with NH₄Cl soln. (20%) (10 ml) and aq. NH₃ (1:4); add hydroxyammonium chloride soln. (10%) (5 ml) and ascorbic acid (0.2 g), dilute to 100 ml and heat to 80° with KCN soln. (10%) (15 ml) and aq. NH₃ (1:1) (15 ml). Add Mg-EDTA soln. (0.05 M) (10 ml) when pptn. begins, cool to 50° and titrate the Mn with 0.02 M EDTA, with Eriochrome black T (0.5%) (0.2 ml) as indicator. Cool the soln., add formaldehyde soln. (8%) (5 ml) to demask the Zn, and titrate with EDTA. K. SAITO

526. Determination of sodium oxide and sodium carbonate in sodium ferrite. N. Ya. Ugnayachev and V. N. Alferova. *Trudy Nauch.-Issled. Inst. Osnov Khim.*, 1958, 11, 310-317; *Ref. Zhur. Khim.*, 1959, (10), Abstr. No. 34,635.—The determination of Na₂O and Na₂CO₃ in sodium ferrite by two methods (*viz.*, treatment with a soln. of NH₄Cl by boiling, and multiple boiling) is studied. It is shown that these methods do not meet the requirements of factory control and cannot be recommended as accurate and rapid methods. A method is evolved which is based on leaching the samples in a special extractor. The accuracy of this method is tested on artificial mixtures of pure Na₂CO₃ and Fe₂O₃, and on ferrites prepared under laboratory conditions by igniting pure Na₂CO₃ and Fe₂O₃. The relative error varies from 0.89 to 3.94% for Na₂O, and from 0.20 to 3.16% for Na₂CO₃. The analysis takes 20 min. C. D. KOPKIN

527. Electrolytic titration of alkaline ferricyanide with hydrazine sulphate and arsenic(III). Suseela B. Sant (Mt. Holyoke Coll., South Hadley, Mass., U.S.A.). *Z. anal. Chem.*, 1959, 188 (2), 112-115 (in English).—Osmic acid catalyses the reaction between Fe(CN)₆³⁻ and As^{III} or hydrazine sulphate so that titrations can be performed at low alkalinity and room temp. (25° to 30°). Sufficient NaOH or KOH is added to an aliquot of K₄Fe(CN)₆ soln. to maintain the alkalinity between 2 and 3 N, together with 2 to 3 drops of osmic acid soln. (0.25 g of OsO₄ in 100 ml of H₂SO₄) (I). Titration with standard hydrazine sulphate soln. is then carried out potentiometrically. Titration with standard arsenous oxide soln. is carried out in a similar way with an alkalinity of 1 to 2 N and 0.1 to 0.2 ml of I as catalyst. The method is rapid and accurate and may also be used for the determination of 0.023 to 0.23 g of hydrazine sulphate or 0.02 to 0.17 g of arsenous oxide. S. M. MARSH

528. Rapid determination of zirconium in ferro-zirconium with cupferron. Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku, Tokyo). *J. Japan Inst. Metals, Sendai*, 1958, 22 (7), 359-362.—Zirconium (20 to 60 mg) reacts quant. and preferentially with cupferron (I) in 20 to 25% H₂SO₄ soln. (100 ml), and the completion of the reaction is indicated by the formation of the Fe-I complex, which gives a yellow soln. in diethyl ether. Interference results from Nb and Ti, which are pptd. together with Zr, and from V, which favours the formation of the Fe-I complex. The determination requires \approx 30 min. *Procedure*—Dissolve the sample (0.1 g) in NH₄F (1 g), H₂SO₄ (1:5) (30 ml) and HNO₃ (1 ml), and heat to white fumes. Cool, add H₃BO₃ (1 g) and heat to white fumes for 5 min.

Add H₂SO₄ (20 ml) and water (80 ml), cool to < 15°, add diethyl ether (30 ml) and titrate with I (8 g per litre, containing 5 g of Na₂CO₃), with vigorous shaking, until the ether layer becomes yellow. K. SAITO

529. Isolation of "structural" constituents in steel. W. Koch and H. Sundermann. *Rader Rdsch.*, 1957, 679-692.—In the electrolytic isolation of structural constituents of steel in neutral electrolytes the pH values in the vicinity of the electrodes vary on account of secondary reactions. The plotting of current density-potential curves in various electrolytes for unalloyed and alloyed steel and for the isolated constituents permits the determination of the most favourable electrochemical conditions for an isolation to be made. Steels dissolve differently in different electrolytes. There are three types of soln. to be differentiated—Fe²⁺-active, Fe²⁺-partly passive, and Fe²⁺-active soln. The frequently necessary preservation of a narrow potential range during isolation has the prerequisite that the geometry of the electrolysis vessels and the electrode surfaces must be considered. This has led to the development of a new electrolysis apparatus and to a theoretical study of the influence of the geometry on the magnitude of the potential. The processes which cause pitting with partly passive soln. and the effect of potential on this type of soln. were studied. Potential differences are closely connected with a more or less intense activation, which can be influenced by the composition of the electrolyte. The mixture of constituents obtained in the isolation can be separated in most cases into several fractions by means of a new magnetic separation process.

CHEM. ABSTR.

530. Chemical analysis of high-alloyed and heat-resistant steel. E. A. Ivanova, N. M. Ivanova, S. I. Kolykhalova, N. M. Smirnova, G. D. Fleisher and A. M. Chernysheva. *Trudy Nauk. Mashinostroit. Zav.*, 1958, (4), 184-188; *Ref. Zhur. Khim.*, 1959, (9), Abstr. No. 31,057.—Procedures are described for determining Nb, W, V, Co, Mn, Al and N in steel. To determine Nb and W, separate the ppt. of tungstic, niobic and silicic acids, remove Si as SiF₄, fuse the residue with a mixture of carbonates and leach the melt with water. Precipitate Nb from the resulting soln. with a mixture of MgCl₂, NH₄Cl and aq. NH₃, and ignite the ppt. to Nb₂O₅; determine the Ti impurity therein photometrically with H₂O₂. Precipitate W with 8-hydroxyquinoline in the filtrate after the removal of Nb, and ignite the ppt. to WO₃. The content of Co, Mn, V, Al and N is determined in separate samples. Titrate V with (NH₄)₂SO₄-FeSO₄-H₂O with phenylanthranilic acid as indicator. To determine Co and Mn, precipitate Fe(OH)₃ and Cr(OH)₃ with ZnO, and precipitate Co with 1-nitroso-2-naphthol and ignite to oxide; then precipitate Mn as MnO₂, oxidise to MnO₄⁻ and titrate with sodium arsenite soln. To determine Al; remove W as tungstic acid, remove Fe, Cr and other metals by electrolysis with a mercury cathode, retain V in soln. with H₂O₂, and precipitate Al with 8-hydroxyquinoline, and ignite to Al₂O₃. Determine N as NH₃, volumetrically. C. D. KOPKIN

531. Flame-spectrophotometric determination of calcium in cast iron. Hidehiro Goto, Shigeo Ikeda and Jin Kimura (Res. Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabiracho, Sendai). *J. Japan Inst. Metals, Sendai*, 1958, 22 (4), 185-187.

—Calcium (up to 0.1%) in nodular cast iron is determined by flame spectrophotometry, most of the Fe being removed by extraction with amyl acetate. Since the presence of 50 to 100 μg of Fe per ml stabilizes the intensity of the flame, Ca is co-pptd. with Fe, by the addition of NaOH and Na_2CO_3 , and separated from P and Al. Manganese ($> 50 \mu\text{g}$ per ml per 4 μg of Ca) increases the blank value at 520 $\text{m}\mu$, and is removed with aq. Br soln. and aq. NH_4 . Silica is removed by treatment with Hf.

K. SAITO

532. Determination of one to five per cent. of boron in steel. J. Janoušek and K. Studlar (Res. Control Inst., Z.V.I.L., Plzeň, Czechoslovakia). *Huin. Listy*, 1959, **14** (5), 458-462.—After a discussion of methods of determining B in steel, the following procedure, which can be completed in 2 hr., is advocated. To the sample (0.5 g) add HCl (1:2) (10 ml) and boil gently under reflux till dissolved. Cool with H_2O and oxidise with 30% H_2O_2 soln. (2 ml) added dropwise with rapid stirring. Boil for 5 min., cool, and dilute the soln. to 50 ml; mix, filter through a dry filter into a dry flask, transfer 25 ml to a separating-funnel and pass it through a column of FN cation-exchange resin (30 cm long \times 1.5 cm diam.) at a rate of 2 to 3 ml per min. Wash the funnel with H_2O (2 \times 10 ml) and then wash the column with 60 ml of H_2O . Combine the eluates, add mixed indicator (0.05 g of methyl red, 0.075 g of bromocresol green, 0.3 g of phenolphthalein and 0.3 g of thymolphthalein dissolved in 100 ml of methanol) and add 5 N NaOH till the soln. is violet. Add HCl (1:1) dropwise till the soln. is pink, boil for 2 min., cool and titrate dropwise with 0.1 N NaOH till green. Add mannitol (4 to 5 g) and titrate the deep red liquid with 0.1 N NaOH through green to violet. Add a further 1 g of mannitol and, if the colour changes, titrate again till violet. Carry out a blank with boron-free steel. The relative error is 0.7%.

J. ŽÝKA

533. Determination of carbon and sulphur in various ferro-alloys with a high-frequency induction furnace. Hidehiro Goto, Toshio Watanabe and Kyohi Suzuki (Res. Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabiracho, Sendai). *J. Japan Inst. Metals, Sendai*, 1958, **22** (5), 233-236.—The use of various ignition accelerators was studied for the volumetric analysis of C and S in ferro-alloys in a high-frequency induction furnace, which enables the sample to be heated rapidly. The best accelerators are as follows: *ferrovanadium*—for C, NiO (0.2 g) and electrolytic iron (I) (1 g) for 1 to 2 g of sample; for S, I (0.2 g) and MnO_2 (0.5 g) for 0.5 to 1 g; *ferrotungsten*—for C, I (1 g) and Cr_2O_3 (0.1 g) for 1 to 2 g; for S, I (0.5 g) for 1 g; *ferromanganese*—for C, Sn (0.5 g), I (1 g) and NiO (0.2 g) for 0.2 to 1 g; for S, NiO (0.2 g) and I (0.3 g) for 1 g; *ferrotitanium*—Sn (0.5 g) and NiO or Cr_2O_3 (0.1 g) for 0.5 g; *haematite and magnetite*—I (1 g for 0.3 g of haematite and 0.5 g for 1 g of magnetite). The procedure is not applicable to ferrosilicon.

K. SAITO

534. Rapid spectrophotometric determination of lead in free-cutting steel. Kazuo Ota and Shigeru Mori (Toyota Motors Ind., Koromo, Aichi-ken). *J. Japan Inst. Metals, Sendai*, 1958, **22** (6), 290-292.—The masking of Fe was improved by a modification in the procedure for the determination of Pb (< 50 mg) with dithizone in benzene. A 10-ml aliquot of the sample soln. (0.5 g in HCl and HNO_3 , diluted

to 500 ml) is transferred to a separating-funnel containing hydroxyammonium chloride soln. (10%) (5 ml), Na K tartrate soln. (10%) (5 ml) and water (20 ml). Masking is thus achieved without heating. The soln. is made alkaline to phenolphthalein and mixed with conc. aq. NH_3 (sp. gr. 0.88) (10 ml) and KCN soln. (5%) (10 ml) and shaken with a soln. of dithizone in benzene ($\approx 0.1\%$) (10 ml). The organic layer is washed with water (10 ml) and diluted to 20 ml, and the extinction is read at 500 $\text{m}\mu$.

K. SAITO

535. Amperometric analysis with cupferron. II. Determination of titanium in steel. Yu. I. Usatenko and G. E. Bekleshova. *Trudy Dnepropetrovsk. Khim.-Tekhnol. Inst.*, 1958, (6), 32-35; *Ref. Zhur. Khim.*, 1959, (9), Abstr. No. 31,003.—The previously described amperometric titration of Ti with cupferron (I), with an anodic current for the oxidation of I at a rotating platinum anode (*cf. Anal. Abstr.*, 1956, **3**, 1301), is used for the determination of Ti in steel. The Ti is first separated from most of the Fe by pptn. with the minimum amount of I. Dissolve 0.2 to 2 g of steel by warming with H_2SO_4 (1:1), and add in the cold 0.5 ml of 0.1 M FeCl_3 (to give an easily collectable Ti-I ppt.) and 5 ml of a 3% soln. of I. Filter off the ppt. and insoluble carbides, wash the residue with cold water, and wash it from the filter, first with hot water and then with hot H_2SO_4 (≈ 10 ml). Boil the soln., add a little $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to oxidise I and evaporate to copious fumes of SO_3 ; dilute with water, add a little aq. NH_3 , then add Na_2SO_3 to destroy the excess of $(\text{NH}_4)_2\text{S}_2\text{O}_8$; boil to remove SO_2 and cool. Insert the electrodes, switch on the motor and apply a potential of 0.58 V; the galvanometer needle goes off the scale, because of the presence of Fe^{2+} . Add a soln. of NH_4VO_3 dropwise to the soln. until the needle returns to zero, then neutralise the soln. to methyl violet with aq. NH_3 (pH 1.0 to 1.5); add 10 ml of a 1% soln. of EDTA (disodium salt) to complex Fe^{2+} , add 3 or 4 g of NaCl and titrate the Ti with a soln. of I, allowing about 1 min. to elapse after each addition of titrant. The method is applicable to the determination of amounts of Ti < 0.001%.

C. D. KOPKIN

536. The spectrophotometric determination of vanadium in iron and steel by the tungstophosphoric acid method. Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *J. Japan Inst. Metals, Sendai*, 1958, **22** (11), 580-582.—The use of HF was examined for masking Fe, Ti and Mo. Although F^- interferes with the coloration of tungstovanadophosphoric acid, this effect is eliminated by increasing the amount of H_3PO_4 and Na_2WO_4 . There is no interference from Ni (< 200 mg for 1 mg of V in 100 ml), Cu (< 200 mg), Co (< 20 mg), Cr (< 0.5 mg), Mn (< 100 mg), Mo (< 100 mg), Ti (< 100 mg), As (< 100 mg), Si (< 100 mg) or HClO_4 . Procedure—Dissolve the sample (0.5 g) in HNO_3 (1:1) (5 ml) and HClO_4 (5 ml), heat to white fumes and remove Cr with HCl. Boil with water (50 ml) for 2 min., cool and add HF (1:10) (20 ml) and H_3PO_4 (sp. gr. 1.7) (5 ml); dilute to 80 ml, heat to 100° and add Na_2WO_4 soln. (16.5 g in 100 ml of water) (10 ml). Maintain at 100° for 5 min., cool, make up to 100 ml and measure the extinction at 440 $\text{m}\mu$.

K. SAITO

537. Radiometric titration of niobium and tantalum in steel. Hiroshi Amano (Res. Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabiracho, Sendai). *J. Japan Inst. Metals, Sendai*, 1958, **22**

(12), 625-628.—The co-pptn. of Ta and Nb with SiO_3 on treatment of the sample with HClO_4 was examined by means of ^{90}Nb and ^{187}Ta and found to be quantitative. A radiometric modification of the titration with cupferron (Elving and Olson, *Anal. Chem.*, 1955, 27, 1817) was also satisfactory under suitable conditions. Tungsten and V must be removed by washing the SiO_3 with aq. NH_3 soln. The sample is dissolved in aqua regia and heated to white fumes with HClO_4 , cooled, treated with SO_2 and filtered. The residue is washed with aq. NH_3 soln., treated with H_2SO_4 and HF , dissolved in oxalic acid and H_2SO_4 , and made up to 100 ml. Several aliquots of this soln. are mixed with the radioactive indicator and varied vol. of cupferron soln., and centrifuged, and the counting rate of the supernatant liquid is measured. The end-point is determined by interpolation. K. SAITO

538. Determination of combined sulphur in steel. A. Fiala and V. Stádler (Z.V.I.L., Plzeň, Czechoslovakia). *Hutn. Listy*, 1959, 14 (5), 462-464.—When determining sulphur combined with Fe and Mn, a preliminary quant. separation of sulphides must be carried out. This can be done by electrolytic dissolution of the steel in a neutral electrolyte containing Na citrate (5%) and NaCl (1%). The isolated material contains silicate and also free MnO_2 , which must be separated. It is stated that the 5-min. boiling of the isolated material with a 17% soln. of glycine, recommended by Klinger and Koch (*Arch. Eisenhüttenw.*, 1938, 11, 569) is not satisfactory and must be repeated with fresh glycine soln. After separating MnO_2 , the residual sulphide is decomposed with HCl, the liberated H_2S is absorbed in a soln. of iodine and the excess of iodine is back-titrated with $\text{Na}_2\text{S}_2\text{O}_3$ soln. *Procedure*—Boil the isolated material (prepared by electrolytic dissolution of 5 to 10 g of steel) with 17% aq. glycine soln. (30 ml) for 5 min. Separate the insol. matter by centrifugation and washing with H_2O and repeat the procedure twice. Transfer the insol. matter with 30 ml of H_2O to a distillation flask, add 34% HCl (3 ml) and distil for 45 min. into 8 ml of 0.02 M iodine; add starch soln. and back-titrate with 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$. Filter the soln. remaining in the distillation flask and wash with boiling H_2O ; to the filtrate and washings add H_2SO_4 (1:1) (5 ml) and evaporate. Cool, add a satd. soln. of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (10 ml) and AgNO_3 soln. (1%) (5 ml), boil, then cool and titrate the MnO_4^- so produced with Na_2AsO_4 soln. The procedure has been tested on steel containing Cu, Ni and Cr. J. ZÝKA

539. Composite spectrophotometric method for determining molybdenum, vanadium and titanium in low-alloy steels. M. Freegarde and B. Jones (Bragg Lab., Naval Ordnance Inspection Estab., Janson St., Sheffield, England). *Analyst*, 1959, 84, 393-396.—The steel (1 g) is dissolved in HNO_3 , H_3PO_4 (3 ml) is added, the vol. is reduced by evaporation, HNO_3 (10 ml) and H_3PO_4 (3 ml) are added and the treatment is repeated until the carbides are dissolved. Any oxidised Mn is reduced with H_2O_2 , the excess of which is removed by boiling, and the liquid is filtered. To one (the blank) of two 20-ml aliquots is added 1 ml of water and to the other 1 ml of H_2O_2 (20 vol.). The extinction of the coloured soln. is measured at 460, 410 and 380 μm against the blank. Equations are given for the determination of the concn. of V, Ti and Mo in the sample, a simplified graphical method is described and also the construction of a slide rule. Reported

results indicate satisfactory accuracy for routine work, the general level for the coeff. of variation being 3%. A. O. JONES

540. Determination of tungsten and molybdenum in high-speed steel. B. E. Jaboulay. *Chim. Anal.*, 1959, 41 (4), 135-136.—By the proposed method W and Mo can be determined in steel containing V. The steel is dissolved by boiling with dil. HCl with addition of HNO_3 and cinchonine. The soln. is filtered and the ppt. of impure WO_3 is ignited and weighed. The ppt. is fused with $\text{K}_2\text{S}_2\text{O}_8$, the melt is dissolved in H_2O and Fe, Cr and Si are ptd. with aq. NH_3 , ignited and weighed. The filtrate contains some Mo. Tartaric acid is added and the soln. made just acid with HCl. The Mo is ptd. with H_2S , ignited and weighed. The original filtrate, which contains the bulk of the Mo, is made alkaline by adding it slowly to a hot soln. of Na_2CO_3 and is then made slightly acid with HCl. The Mo is ptd. as PbMoO_4 by the addition of $\text{Pb}(\text{NO}_3)_2$ in the presence of NH_4Cl , Na acetate and Na formate. The ppt. is ignited and weighed. G. BURGER

541. Determination of cobalt, iron and vanadium or manganese in soft magnetic alloys. D. H. Wilkins and L. E. Hibbs, jun. (Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, 20 (5), 427-429.—The separation of Fe and V (or Mn) from Co is effected by passing an aliquot of the sample soln. in 9 N HCl through a column of Dowex-1 resin (100 to 150 mesh, chloride form) and then eluting, in succession, V or Mn with 9 N HCl, Co with 4 N HCl, and Fe with 0.5 N HCl. After concentrating each eluate, adding acetate buffer and an excess of EDTA (disodium salt), the pH is adjusted to ≈ 4.8 (Mn to pH 7) and ≈ 150 ml of H_2O is added. Each soln. is then back-titrated, under u.v. light, with standard copper soln. to the quenching of the fluorescence of the indicator (0.1% calcein in 0.001 N NaOH). W. J. BAKER

542. Comparative photometric determinations of cobalt in aluminium and its alloys. H. Pohl (Bundesanst. f. Materialprüfung, Berlin-Dahlem). *Aluminium*, Berlin, 1959, 35 (6), 260-261.—The sample (1 g) is dissolved in 25% NaOH soln. (60 ml) with 1 ml of H_2O_2 soln., then boiled for 10 min., diluted to 200 ml and filtered hot. The residue is dissolved in HCl and bromine water and transferred to a 100-ml flask; ZnO is added and the mixture is diluted to vol. The soln. is filtered and 20 ml is transferred to a 100-ml flask with NaCl_2 soln. [10 ml, 15% in HCl (sp. gr. 1.19)] and diluted to vol. with HCl (sp. gr. 1.19). A second aliquot is treated similarly but diluted to vol. with water. After 10 min. the extinction is determined in 50-mm cells at 578 μm (extinction = 0.25 for 20 mg of Co per 100 ml). Beer's law is obeyed up to 20 mg of Co per 100 ml. The results obtained are comparable with those by a nitroso-R-salt method (cf. Guerin, *Analyst*, 1956, 81, 409). Up to 300 mg of Ni, 50 mg of Fe, 30 mg of Cu or Zn, 20 mg of Si or 1 mg of Ti, V, Mo, Mn or Cr does not interfere. T. R. ANDREW

543. Simultaneous spectrophotometric determination of trace amounts of cobalt, nickel and copper with NN'-bis-(3-dimethylaminopropyl)dithio-oxamide. W. D. Jacobs and J. H. Yoe (Dept. of Chem., Univ., Charlottesville, Va., U.S.A.). *Anal. Chim. Acta*, 1959, 20 (5), 435-443.—The procedure given is based on the formation of the Co, Ni and

Cu complexes of $\text{NN}'\text{-bis-(3-dimethylaminopropyl)}$ -dithio-oxamide. The complexes are formed with the reagent ($0.0015 M$ in ethanol) (3 ml) at pH 9 ± 0.3 , in the presence of 0.1% gum acacia soln. (4 ml) to keep the complexes in soln. After 30 min. the soln. is diluted to 25 ml and the respective max. extinctions are measured at $500 \text{ m}\mu$ (for Co), $430 \text{ m}\mu$ (for Ni) and $365 \text{ m}\mu$ (for Cu) against a reagent blank. Beer's law is valid for all three systems over the range of 0.16 to 4 p.p.m. The sensitivities ($\mu\text{g per sq. cm.}$) are 0.0045 (for Co), 0.0077 (for Ni) and 0.0039 (for Cu); these are comparable with those for the respective complexes with dithio-oxamide (Jacobs and Yoe, *Ibid.*, 1959, **20**, 332). When Al^{3+} , Fe^{3+} and Mn^{2+} are present, e.g., in an alloy, they should either be removed or complexed to prevent their interference. The accuracy of the method is satisfactory. W. J. BAKER

544. New sensitive method for the detection of nickel. V. Armeanu, D. Camboli and C. Iancu (Politech. Inst., Bucharest). *Bul. Inst. Polit. Bucuresti*, 1958, **20** (2), 81-84 (in French).—Bivalent Ni gives a beige ppt. with β -furil monoxime (I). The sensitivity of the reaction depends on the order in which the reagents are added. *Procedure*—A drop of test soln. is dried on filter-paper; one drop of a 1% ethanolic soln. of I is added, and the spot is exposed to NH_3 vapour; Al^{3+} , Cr^{3+} , Sn^{4+} , Sn^{2+} , Sb^{3+} , Sb^{5+} , AsO_3^{3-} and AsO_4^{4-} interfere if present in concn. > 10 times, Bi^{3+} at concn. > 30 times, and Hg^{2+} at concn. > 250 times, that of Ni^{2+} . The limit of detection is $0.32 \mu\text{g}$ of Ni, and the dilution limit is 1 in 2×10^5 . H. SHER

545. Analysis of nickel. I. Chemical methods. T. R. Andrew and C. H. R. Gentry (Material Res. Lab., Mullard Radio Valve Co. Ltd., Mitcham Junction, Surrey). *Metallurgia, Manch.*, 1959, **60** (357), 27-30; (358), 69-72; (359), 121-124; (360), 173-176.—A critical survey is given of published methods for the chemical determination of alloying constituents and impurities in electronic nickel. Detailed instructions for carrying out specific methods for C, Al, Cr, Co, Cu, Fe, Mg, Mn, Si, S, Ti and W are given with statements of the time required and the precision attainable. (261 references.) N. E.

546. A very selective determination of nickel with cyclohexane-1:2-dione dioxime [nioxime]. D. Monnier and W. Haerdi (Univ., Geneva, Switzerland). *Anal. Chim. Acta*, 1959, **20** (5), 444-455 (in French).—Nickel can be separated from a large excess of other ions (Co^{2+} , Cu^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} , Ca^{2+}) by pptn. as its complex with nioxime (I) in aq. soln. at pH 3.5, followed by the almost quant. extraction of this ppt. into benzene to remove some co-pptd. Co and Fe. After centrifuging, the aq. phase is removed, and the benzene suspension is treated with 5*N* HCl to dissolve the complex; the Ni in the aq. phase can then be determined colorimetrically by the method of Ferguson and Banks (*Anal. Chem.*, 1951, **23**, 448). If high concn. of Co are present, e.g., as in a sample of cobalt salt(s), the bulk of the Co should be removed by an initial extraction with KSCN from 5*N* HCl into ethyl acetate, a modification of Kirk's apparatus being used for this. The Ni-I complex can also be dissolved directly in quinoline (satd. with H_2O) at $\approx 80^\circ$ and, after centrifuging, the extinction of the organic phase is measured at $\approx 430 \text{ m}\mu$. Beer's law is valid for 2 to 35 μg of Ni per 5 ml of soln.; the sensitivity is 0.12 μg or one-quarter that for the

Ferguson and Banks method, which, however, has certain limitations. The max. error is $\pm 3\%$; a duplicate analysis takes ≈ 1 hr. W. J. BAKER

547. Determination of nickel in beryllium compounds. U.K.A.E.A. (Res. Group, H.M. Gun Wharf, Chatham, Kent). AERE-AM 54, 1959, 4 pp.—The method is based on standard analytical practice and is written with full details by J. Walkden.

548. Colorimetric determination of platinum in catalysts. Ya. E. Shmulyakovskii. *Khim. i Tekhnol. Topliv i Maset*, 1958, (12), 56-58; *Ref. Zhur., Khim.*, 1959, (10), Abstr. No. 34,617.—The simple, rapid and accurate method described is based on the photometry of $[\text{PtSnCl}_4]^{4-}$. The procedure for the preliminary chemical treatment of the catalyst is considerably simplified. Ignite 0.2 to 0.3 g of ground catalyst (Pt on $\gamma\text{-Al}_2\text{O}_3$) for 30 min. at 1100° to convert the $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$. Evaporate 0.1 g of the ignited catalyst once with 5 ml of aqua regia and three times with 1 ml of HCl (1:1), dilute the residue with HCl (1:24) to 100 ml and filter off the $\alpha\text{-Al}_2\text{O}_3$ on a No. 3 or 4 sintered crucible. To 20 ml of the filtrate add 1 ml of a 10% soln. of SnCl_4 in conc. HCl and measure the extinction with a blue filter. Beer's law is obeyed for concn. of Pt $> 5.5 \mu\text{g per ml}$. The parallel determination of Pt in 3 or 4 samples takes 4 to 5 hr.; the maximum error is 0.01% (abs.). The method may be used for controlling the production of platinum catalysts.

C. D. KOPKIN

549. Determination of platinum in the cathode slime during the production of hydrogen peroxide. M. Struszynski and J. Chwastowska (Anal. Chem. Dept., Technol. Inst., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 949-964.—After separation of the bulk of the Pb by pptn. of PbCl_2 , the soln. is treated with HCl and NaCl and the chloroplatinate is reduced by SnCl_4 to chloroplatinite, which is extracted with diethyl ether and measured colorimetrically. The error is $> 5\%$ for concn. of Pt of $\approx 0.2\%$. H. DMOWSKA

550. Determination of platinum in Perhydrol and ammonium fluoride by extraction titration. W. Kemula, W. Brachaczek and A. Hulanicki (Phys. Chem. Dept., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 913-921.—Traces of Pt ($\approx 0.0015\%$) are determined by extraction titration with 0.001% dithizone in CCl_4 . The interference of Cu, Fe, Pb and Al is eliminated by the addition of an excess of SnCl_4 . The coeff. of variation is $\pm 4\%$ for concn. of Pt from 0.0009 to 0.0028%. H. DMOWSKA

See also Abstracts— 339. Thenoytrifluoroacetone as a reagent. 340. *o*-Carboxyphenylazo-1:8-dihydroxynaphthalene-3:8-disulphonic acid (sodium salt) as a reagent. 342. Magnetometric titration. 616. Determination of Cl in coal. 629. Determination of $\text{K}_2\text{S}_2\text{O}_8$ in synthetic latex. 637. Determination of ^{88}Sr in biological materials. 638. Determination of ^{88}Sr in bones. 734. Separation of ^{88}Sr from Ca. 776. Silicon in water. 777. Nitrates in water. 778. Phosphates in water. 780. Uranium and thorium in water. 797. Gases in liquid metals. 826. Electrode for spectrography. 834. Determination of HF in gases.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives, etc.

551. Simultaneous micro-determination of carbon, hydrogen and nitrogen in nitrogenous compounds. V. A. Klimova and K. S. Zabrodina (Inst. Organ. Chem. "N. D. Zelinskii," Acad. Sci. USSR). *Izv. Akad. Nauk SSSR*, 1959, (4), 582-585.—Details are given of an apparatus designed for the micro-analysis of compounds containing C, H, N, O, Cl and Br. The substance (2 to 8 mg) is slowly vapourised at 200° to 350° (according to its b.p.) in a quartz dish contained in a long combustion tube surrounded by a detachable electric heater. The dish is then moved along the combustion tube to within a few cm of a section plugged with platinum gauze (also silver gauze if halogens are present) heated to 800° to 835° by a second electric heater; O is passed through the tube at the rate of 5 to 8 ml per min. The H₂O formed is absorbed by anhydride, the oxides of N are absorbed by 0.02 M K₂Cr₂O₇ in H₂SO₄ (sp. gr. 1.84) deposited on silica gel, and CO₂ is absorbed at the outlet of the apparatus by Ascarite. To prevent the condensing H₂O from trapping NO₂ at the inlet of the water-absorber, the water-absorber is heated to 75° to 85° with a detachable electric heater. Results are accurate to within ± 0.2% for C and H and ± 0.3% for N.

K. R. C.

552. Simultaneous determination of carbon, hydrogen and halogens. V. A. Klimova and E. N. Merkulova (Inst. Org. Chem. "N. D. Zelinskii," Acad. Sci. USSR). *Izv. Akad. Nauk SSSR*, 1959, (5), 781-786.—A quartz dish (70 to 80 mm) containing 0.4 to 0.7 g of electrolytic silver (prep. described) is placed at one end of a long combustion tube where it is heated to 410° to 440°; the dish is later pushed along to another section of the tube where it is heated to 900° to 950°. The apparatus and method used, with minor modifications, are those of Korshun and Sheveleva (*Zhur. Anal. Khim.*, 1956, **11**, 376); H₂O and CO₂ are absorbed by anhydride and Ascarite, respectively. Carbon, H and halogens are determined with an error > ± 3%. The method can be used for the analysis of organic silicon and organic boron compounds. The presence of N does not cause interference.

K. R. C.

553. Direct determination of oxygen in organic substances. [Application to sulphur-containing compounds.] W. Radmacher and A. Hoverath (Brennstoffchem. Inst. d. Ruhrkohlen-Beratung G.m.b.H., Essen). *Z. anal. Chem.*, 1959, **167** (5), 336-342.—In the Unterzacher procedure for the determination of O by the reaction of the liberated CO with anhydro-iodic acid (HIO₃.I₂O₅) to give CO₂ (cf. *Anal. Abstr.*, 1957, **4**, 914), sulphur compounds interfere seriously, owing to the formation of CS₂ and its subsequent oxidation to CO₂. By using a tube, heated by a Bunsen burner and packed with copper, immediately after the reaction furnace this interference is almost completely eliminated.

T. R. ANDREW

554. Determination of phosphorus in organic compounds. U. Bartels and H. Hoyme (Dtsch. Akad. der Wissenschaften zu Berlin). *Chem. Tech.*,

Berlin, 1959, **11** (3), 156-157.—A comparative study is made of the merits of available methods for the semi-micro determination of P in fabrics flame-proofed with organic phosphorus compounds. For the sample decomposition, the method of Schöniger (*Mikrochim. Acta*, 1956, 869) was useful when the phosphorus content was > 5%; below this level the method of Bolin and Stemberg (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 345) gave more accurate results. For the final determination of phosphate, the complexometric method of Flaschka (relative standard deviation 0.08%, as compared with 0.59% gravimetrically) and the molybdate method of Lorenz are best. The test substances used were triphenylphosphine and recrystallised chloromethyl-phosphonic acid. The proofed fabrics tested were rayon and cotton.

L. M. RIEGELHAUPT

555. Determination of sulphur in organic compounds by benzidine hydrochloride. Tseng-Gee Sun and Teng-Han Tang. *Acta Pharm. Sinica*, 1958, **6**, 228-232.—Fuse a sample (containing 30 to 75 mg of SO₄²⁻) carefully in a nickel crucible with KNO₃ (1 g) and KOH (8 g), leach with water, acidify with HCl and heat gently until the evolution of bubbles ceases. Filter the soln., dilute to about 60 ml, and adjust the pH to 2 to 3 by first neutralising with 6 N aq. NH₃ and then adding 0.2 ml of 6 N HCl. Warm the soln. to 70° and treat with benzidine hydrochloride soln. (8 g per litre) (50 ml) to precipitate the SO₄²⁻ as benzidine sulphate (I). Cool in ice for 1 hr., filter off the ppt. with glass powder and wash with satd. I soln. (4 × 5 ml). Dissolve the ppt. in 50 ml of water at 80° and titrate with 0.1 N NaOH to phenolphthalein. Results agree with those obtained by the gravimetric method for the following compounds—3-(methylthio)alanine, 7-chlorothiochromanone, 5-bromo-8-methylthiochromanone, cystine, sulphaniilic acid, sulphosalicylic acid, sulphaniilamide, 2-mercapto-N-naphthylacetamide and cysteine with an average error of ± 0.11%.

CHEM. ABSTR.

556. Rapid determination of sulphur in organic compounds. L. Gildenberg (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Microchem. J.*, 1959, **3** (2), 167-171.—The procedure is based on the Schöniger combustion method (cf. *Anal. Abstr.*, 1955, **2**, 1816; 1957, **4**, 924). After combustion of the sample, the S is absorbed in bromine water and the soln. titrated amperometrically with standard Pb(NO₃)₂ soln. The mean relative deviation for all compounds analysed (S content ranging from ≈ 11 to 27%) was ± 1%. A determination may be completed in < 90 min. The only interference experienced was from PO₄³⁻ which react with the titrant.

D. F. PHILLIPS

557. Spectrophotometric method for the determination of small amounts of sulphur in organic compounds: a semi-micro and micro method. I. Lysy and J. E. Zaremba (Food Machinery and Chem. Corp., Central Res. Lab., Chem. Div., Princeton, N.J., U.S.A.). *Microchem. J.*, 1959, **3** (2), 173-180.—A rapid method is described which combines the simplicity of oxygen flask combustion (cf. *Anal. Abstr.*, 1958, **5**, 2663) with the efficiency of a spectrophotometric finish (with barium chloranilate at pH 4). The method is suitable for the determination of S in the presence of negative elements (e.g., Cl, P and N) without separation. Average recoveries of 99.46 ± 0.94% were obtained for organic compounds containing from ≈ 5 to 42% of S and of 100.38 ± 0.95% for P-containing

compounds with sulphur contents between ≈ 11 and 35%. The method is also suitable for trace amounts of S (0.05 to 0.5%) with samples of 20 to 50 mg.

D. F. PHILLIPS

558. Determination of halogen in halogen-substituted organic compounds. A. A. Bugorkova-Zelentskaya and L. N. Petrova (All-Union Sci. Res. Inst. of Synth. and Natural Perfumes, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (3), 381-382.—In many cases chlorine cannot be accurately determined in aliphatic halogen-substituted organic acids by reduction with skeletal nickel catalysts in an aq. ethanolic-alkaline medium, and another procedure is proposed. Add *N* NaOH (20 ml) in 50% aq. ethanediol to the test substance (0.1 g). Heat the reaction mixture on a sand bath for 1.5 hr., neutralise it, acidify with HNO_3 , and titrate the chlorine by the Volhard method. Recoveries vary between 98-23% (chloroacetic acid) and 100-87% (9-chlorononanoic acid).

K. R. C.

559. Apparatus and procedure for the combustion of a wide range of samples of organic substances. (Determination of fluorine, chlorine, bromine, iodine, sulphur and boron.) F. Martin and A. Floret (Soc. des Usines Chim. Rhône-Poulenc, Vitry-sur-Seine). *Chim. Anal.*, 1959, **41** (5), 181-185.—The technique described previously (*ef. Anal. Abstr.*, 1959, **6**, 197) has been adapted to the determination of small concn. of S or halogen impurities in solid samples ranging in wt. from several milligrams to ≈ 1 g. The organic compound is pyrolysed in a stream of pure H₂ and the gaseous mixture is then burnt at the end of a quartz tube (acting as a blowpipe) in a stream of O₂. The water-vapour formed contains the bulk of the impurity and, after condensation, is collected in a flask containing a known vol. of a standard soln. that will absorb the impurity being determined, *e.g.*, NaOBr for S, NaOH for Cl and F, Na formate for Br, and an acetic acid soln. of Na acetate for I. To ensure complete removal of B from the sample, the stream of H₂ should be mixed with methanol vapour; the absorbent is H₂O. No quant. data are given.

W. J. BAKER

560. Micro-determination of iodine in organic compounds. H. Urrutia, A. Ramírez and N. Aguayo (Inst. de Quím. Orgán., Univ. Concepción). *Bol. Sci. Chil. Quím.*, 1958, **8** (1-2), 9-11.—The method is based on the conversion of organic iodine into inorganic iodide by fusion with Na₂O₂ and ethanediol in a Wurzschnitt bomb. The contents of the bomb are treated with 25 ml of water, heated to decompose the excess of peroxide, and then heated to 100° with 1 g of hydrazine sulphate for 1 hr. The soln. is then cooled, neutralised with 10 ml of 7*N* HNO₃ and diluted to 100 ml. A 20-ml aliquot is adjusted to pH 6.2 to 6.4 and titrated with 0.01*N* mercuric nitrate to a permanent rose-violet colour, with 1 ml of 0.1% ethanolic diphenylcarbazone soln. as indicator. The method is claimed to be simpler and more accurate than other currently used methods.

E. C. APLING

561. Micro-determination of carbonyl groups using sodium borohydride. (Preliminary communication.) M. Sobotka and H. Trutnovsky (Inst. for Org. and Pharm. Chem., Univ., Graz, Austria). *Microchem. J.*, 1959, **3** (2), 211-213.—Sodium borohydride (**I**) reduces the carbonyl group to the hydroxyl group (*ef.* Chaikin and Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 122) and its use as a general reagent for determining carbonyl groups is studied.

After reduction of the compound with a known quantity of **I**, the hydrogen liberated from the excess of **I** on the addition of an acid is measured. Preliminary experiments were carried out with the Solty's apparatus (*Mikrochemie*, 1936, **20**, 107), and a special reaction vessel based on the Lindberg and Misiorny apparatus (*Svensk Papp-Tidn.*, 1952, **55**, 13) was used later. Preliminary results are quoted.

D. F. PHILLIPS

562. Determination of methoxyl groups. Hiroshi Sobue, Akira Hatano and Toshiaki Arai (Tokyo Univ., Japan). *J. Soc. Text. Cellulose Ind., Japan*, 1959, **15**, 21-23.—The use of AgNO₃ soln. as an absorbent in the Zeisel method is impracticable when the samples contain sulphur compounds. In a modified method, methyl iodide is absorbed in pyridine and is decomposed with the formation of a methyl iodide-pyridinium salt, which has a max. extinction at 366 m μ . Since the extinction increases with the content of methoxyl group, the methoxyl value in samples is rapidly and accurately determined by the extinction at 366 m μ . The molar extinction coeff. of the methyl iodide-pyridinium salt is 6.2×10^4 .

CHIM. ABSTR.

563. Spectrophotometric method for the determination of organic compounds by near infra-red absorption. Ts. N. Roginskaya and A. I. Finkel'stein. *Zhur. Anal. Khim.*, 1959, **14** (3), 360-361.—Mixtures of organic compounds can be determined (by calibration curves) with near i.r. absorption spectra at 1 to 2 μ obtained with a UM-2 monochromator, with a germanium photo-element. The cells are glass tubes (diam. 30 mm and length 200 mm) the preparation of which is described in detail, the thickness of the absorbing layer is 10 mm and the light filter is an ethanamine complex of Cu. The circuit is described in detail. The mean relative error for 15 Chlorex ($\beta\beta'$ -dichloroethyl ether) determinations in dichloroethane in the concn. range of 5 to 40% is $\approx 7\%$. In the determination of H₂O in isopropyl alcohol the limit of sensitivity is $\approx 1\%$ and the mean relative error for 10 determinations is $\approx 2.5\%$, which is similar to the error for photometric determinations. In the determination of cyclohexanol in cyclohexanone, the limit of sensitivity is $\approx 5\%$ and the mean relative error is $\approx 4\%$. In all cases the determinations take 5 to 10 min.

K. R. C.

564. Measurement of carbon-14 and hydrogen-3 in the gas phase. H. Simon, H. Daniel and J. F. Klebe (Org.-chem. Inst. Tech. Univ., Berlin-Charlottenburg). *Angew. Chem.*, 1959, **71** (9), 303-308.—These isotopes in labelled organic compounds are best determined in a flow counter. The sample (3 to 60 mg) is mixed with 10 times its weight of KClO₄ and sealed in a glass bomb at a pressure of 0.1 torr. After fusion and reaction by heating to 605° for 40 min. the specimen is allowed to cool. The bomb is opened in a vacuum system and the CO₂ is pumped off and counted. Amalgamated zinc is added to the residue, the bomb is again sealed and heated, and the H evolved is subsequently pumped off and counted.

T. R. ANDREW

565. Gas-chromatographic analysis of C₁ to C₄ hydrocarbons by magnesium silicate. V. Crespi and F. Cevolani (Ist. Donegani Soc. Montecatini, Novara, Italy). *Chim. e Ind.*, 1959, **41** (3), 215-217.—The separation of C₁ to C₄ hydrocarbons (both saturated and unsaturated) has been carried out.

with satisfactorily short retention times, in a 1 to 2-metre column packed with magnesium silicate (preparation described) at 22°, with H as carrier gas. Good separations of propadiene from butane and of but-1-ene from 2-methylpropene are obtained. The low temp. prevents the polymerisation of 2-methylpropene and butadiene. The analysis of gases containing CO₂ and acetylene, and the separation of *cis*- and *trans*-but-2-ene cannot be carried out by this method.

L. ZANONI

566. Gas-chromatographic analysis of hydrocarbon streams from butane hydrogenation. T. A. McKenna, jun., and J. A. Idleman (Firestone Tire and Rubber Co., Orange, Tex., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1021-1023.—Procedures are described for the separation and analysis of H and hydrocarbons up to C₆; columns at room temp. were used. Separations are sufficiently complete for peak height - half band-width calculations to be made on all components without resorting to calibration factors.

G. P. COOK

567. Analytical applications of far-infra-red spectra. II. Spectra-structure correlations for aliphatic and aromatic hydrocarbons in the caesium bromide region. F. F. Bentley and E. F. Wolfarth (Wright Air Dev. Center, Wright-Patterson Air Force Base, Ohio, U.S.A.). *Spectrochim. Acta*, 1959, (3-4), 165-205.—The spectra of approx. 400 alkanes, alkenes, cyclopropanes, cyclopentanes, cyclohexanes, substituted benzenes, naphthalenes and biphenyls have been studied in the region 15 to 35 μ . The skeletal bending frequencies of the alkanes and alkenes and the non-planar bending frequencies of the aromatics are the most useful for qual. analysis. (53 references.) P. T. BEALE

568. Gas-chromatographic analysis of various mixtures of compounds containing chlorine. G. W. Warren, L. J. Priestley, jun., J. F. Haskin and V. A. Yarborough (Union Carbide Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1013-1016.—Chromatographic methods are described for the analysis of unrefined 1,2-dichloroethane, refined CCl₄ and CHCl₃, and refined 1-chlorobutane. Columns of paraffin wax-Celite 545 are used and are operated at different temp. for each material. Reasonable agreement with the results obtained by other methods was attained.

G. P. COOK

569. Analysis by preparative vapour-phase chromatography and mass spectrography of the heavy products of the pyrolysis of chlorodifluoromethane. J. Serpinet (Centre de Rech. de Lyon de la Soc. d'Electrochim., d'Electrométall. et des Acieries Elect. d'Ugine). *Chim. Anal.*, 1959, 41 (4), 146-151.—In the manufacture of tetrafluoroethylene the pyrolysis of CHClF₃ yields a gaseous mixture of chloro and fluoro compounds representing 5% to 10% of the reaction products. This mixture was fractionated by vapour-phase chromatography in a stainless-steel column (3 metres long by 20 mm diam.) with dibutyl phthalate as the stationary phase and H as carrier gas. The fractions were collected in liquid-air traps. Each fraction was examined in a mass spectrometer. Products representing \approx 98% of the sample were identified and determined.

G. BURGER

570. Gas-chromatographic determination of inert gas components in refrigerants. H. Kelker (Anal. Lab. der Farbwerke Hoechst A.-G., Frankfurt/M.).

Kalletechnik, 1959, 11 (4), 101-103.—A procedure is described for the determination of very small concn. (\approx 0.02% by vol.) of gases, e.g., CO, N and O, in Frigen 12 (CCl₂F₂). Silica gel is used as the stationary phase and hydrogen as the carrier gas. The accuracy is within 1 to 3% (relative), and the method is suitable for process and dispatch control.

W. H. KEMP

571. Organic analysis. XIII. Estimation of hexoses with 5-hydroxy-1-tetralone. Tsutomu Momose and Yosuke Ohkura (Pharm. Inst., Med. Fac., Univ. of Kyushu, Japan). *Chem. Pharm. Bull. Japan*, 1959, 7 (1), 31-34 (in English).—The method is based on the formation of a fluorescent compound when a hexose is heated with 5-hydroxy-1-tetralone (I) in H₂SO₄. *Procedure*—To 1 ml of aq. soln. containing 1 to 40 μ g of hexose are added 1 ml of a 0.1% soln. of I in conc. H₂SO₄ and 3 ml of H₂SO₄ while cooling in ice. The reactants are mixed and heated for 40 min. on a water bath, cooled in ice-water and diluted with 15 ml of water. After setting aside the soln. at 15° to 25° for 30 min., the intensity of fluorescence at 532 $\text{m}\mu$ is measured under excitation with u.v. radiation of 365 $\text{m}\mu$ against a reagent blank. The effect of concn. of reagents is studied. Pentoses do not produce a fluorescence under these conditions, but a very high concn. of xylose slightly depresses the fluorescence due to glucose. Different hexoses give different fluorescence intensities.

E. J. H. BIRCH

572. Paper-chromatographic detection of glucose, fructose and mannose in mixtures. E. Pfeil, A. Baier and O. Balzer (Chem. Inst., Univ. Marburg/L., Germany). *Angew. Chem.*, 1958, 70 (22-23), 702.—By the use of the solvent mixture ethyl acetate - pyridine - water (7:2:1) a satisfactory separation of glucose (*R_f* 0.26) and mannose (*R_f* 0.36) is achieved. Fructose accompanies the mannose, but a small addition of diphenylborinic acid - aminoethanol (Flavognost-Heyl) (I) increases the *R_f* value of fructose without seriously affecting the aldoses. *R_f* values of other carbohydrates after the addition of I are given.

N. E.

573. Determination of carbonyl compounds by reaction with amines. L. N. Petrova, E. N. Novikova and A. B. Skvortsova (All-Union Sci. Res. Inst. of Synthetic and Natural Perfumes, Moscow). *Zhur. Anal. Khim.*, 1959, 14 (3), 347-351.—The measurement of the amount of H₂O produced in the quant. reaction between amines and aldehydes can be used for the determination of the aldehydes. *Procedure*—Add a 15% soln. (5 to 10 ml) of *o*-toluidine or aniline in benzene to the aldehyde (0.2 to 0.4 g) and titrate with Karl Fischer reagent. Subtract the moisture content of the original aldehyde. Alternatively, add a 15% soln. (15 ml) of aniline in benzene to the aldehyde (0.15 to 0.4 g), distil off the water and determine by the Karl Fischer method. The results are in good agreement with those obtained by the method of oxime formation.

K. R. C.

574. Separation of micromole mixtures of 2:4-dinitrophenylhydrazones. W. G. Jennings (Univ. of California, Davis, U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1117-1118.—The method described by Monty (*cf. Anal. Abstr.*, 1959, 6, 213), in which 2:4-dinitrophenylhydrazones are separated chromatographically on Hyflo Super-Cel activated with nitromethane as the stationary phase, and light petroleum satd. with nitromethane as the developing

solvent, was extended and modified to include carbonyl compounds encountered in the analysis of flavouring materials. The relative elution rates of 21 carbonyl compounds with respect to *n*-pentanal are listed.

G. P. COOK

575. Determination of aldehydes by the method of oxime formation. L. N. Petrova and E. N. Novikova. *Trudy Vses. Nauch. Inst. Sintetich. i Natural'n Dushist. Veshchestv.* 1958, (4), 78-82; *Ref. Zhur. Khim.* 1959, (8), Abstr. No. 15,119. *Procedure*—Add 0.5 N hydroxyammonium chloride (I) in 60% ethanol (20 ml) to the sample containing 5 to 6 millimoles of aldehyde. Titrate the HCl produced with 0.5 N NaOH in the presence of methyl orange. For a stereoisomeric aldehyde use 1 to 2 N I, e.g., in the production of the oxime of α -methyl-*p*-isopropylcinnamaldehyde use N I in 85% ethanol and titrate the ethanolic soln. in the presence of bromophenol blue. The results for the determinations of several aldehydes are given, including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, heptanal, decanal, citral, citronellal, hydroxycitronellal, benzaldehyde, vanillin, 2-methyl-3-methoxybenzaldehyde, piperonal, β -anisaldehyde, salicyaldehyde, cinnamaldehyde and hydrocinnamaldehyde. The conditions are given for the determination and the results of the determination of citronellal in the presence of citronellal and ethanol, phenylacetaldehyde and substituted cinnamaldehydes, e.g., α -pentylcinnamaldehyde (jasmine aldehyde) and α -methyl-*p*-isopropylcinnamaldehyde.

K. R. C.

576. Analysis of aldehydes. II. Iodimetric determination of glyoxal by means of its α -hydroxy-sulphonate (aldehyde bisulphite). E. Schulek and L. Maros (Inst. for Inorg. and Anal. Chem., L. Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.* 1959, 65 (5), 195-197.—Glyoxal (I) is converted into glyoxal bisulphite (II); after destroying the excess of bisulphite, II is converted into glyoxime by means of hydroxylamine, and the sulphite that is formed simultaneously is titrated with iodine in acid medium. Pentane (III) is used to exclude air. *Procedure*—Dissolve II (0.65 to 0.70 g) or an \approx 30% soln. of I (0.35 to 0.40 g) in H_2O (100 ml). Into a 100-ml stoppered flask place 5% Na_2SO_3 soln. (3 ml) and 1 drop of methyl red soln.; neutralise with 10% acetic acid and add 1 ml in excess. Then add the soln. of I or II (10 ml), dilute to \approx 30 ml with water and add III (5 ml). After 30 min., add 10% acetic acid (2 ml), followed by 1% starch soln. stabilised with 0.1% salicylic acid (10 drops). Destroy most of the excess of H_2SO_4 with 5% iodine soln. and finally titrate with 0.1 N iodine till the blue colour persists for \leq 30 sec. after shaking. After III separates add 10% hydroxyammonium chloride soln. (2 ml) and 20% NaOH soln. (5 ml). After 5 min., neutralise with 20% HCl and add 2 ml in excess. With slow mixing, titrate the soln. with 0.1 N iodine; at the end-point, stopper the flask and shake it vigorously. The accuracy is within $\pm 0.5\%$. Oxidising or reducing agents do not interfere.

A. G. PETO

577. Gas-chromatographic analyses of products from aldol condensations. G. W. Warren, W. J. Lambdin, J. F. Haskin and V. A. Yarborough (Union Carbide Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1016-1019.—Gas-chromatographic methods are described for the analysis of the products of three different aldol condensations, *viz.*, acetaldehyde with butyral-

aldehyde, isobutyraldehyde with butyraldehyde, and isobutyraldehyde with propionaldehyde. The major components of these mixtures can be determined with a precision of $\approx \pm 4\%$. The limits of detection vary from ≈ 100 p.p.m. for butyraldehyde to 1000 p.p.m. for 2-ethylhex-2-enal.

G. P. COOK

578. Simultaneous spectrophotometric determination of ethyl methyl ketone and ethyl acetate. M. Freegarde and B. Jones (Bragg Lab., Naval Ordnance Inspection Estab., Janson St., Sheffield, England). *Analyst*, 1959, 84, 396-397.—The method was devised to determine the relative amounts of the two liquids in a mixture used as the solvent base for a liquid rubber. An aliquot (2 ml) of the distillate from the liquid rubber is diluted to 20 ml with cyclohexane. After thorough mixing, a 2.5-ml aliquot is diluted to 50 ml with cyclohexane. The extinction of this liquid is measured at 280 and 220 m μ against cyclohexane. The measurements are then related to the cor. cn. of the two components by comparison with calibration measurements made on soln. of mixtures of the pure liquids. The method is applicable to solvent mixtures containing $> 30\%$ of ethyl acetate, and the results agree satisfactorily with those of a chemical method.

A. O. JONES

579. Conductimetric titration of very weak acids. F. Gaslini and L. Z. Nahum (Res. Div., Vita Mayer & Co., Milan, Italy). *Anal. Chem.*, 1959, 31 (6), 989-992.—Weak acids, particularly phenols, can be titrated conductimetrically in a weak nitrogenous base (e.g., aq. NH_4) by using LiOH as titrant. The intersection angles obtained are as satisfactory as those given by strong acids when the usual conductimetric methods are employed. Mono- and poly-basic acids gave accurate and reproducible results, which were in good agreement with those obtained by the method of Fritz (cf. *Brit. Abstr. C.* 1952, 337).

G. P. COOK

580. Review of the characterisation and determination of acids and acid anhydrides. S. Veibel (Tech. Univ., Copenhagen). *Chim. Anal.*, 1959, 41 (2), 49-53.—A review is given of methods for the determination of carboxylic acids, anhydrides and esters. (64 references.)

S. M. MARSH

581. Non-aqueous titration of organic acids, anhydrides, acyl halides, strong inorganic acids and reactive alkyl halides in various mixtures. A. Patchornik and S. E. Rogozinski (Weizmann Inst. of Sci., Rehovoth, Israel). *Anal. Chem.*, 1959, 31 (6), 985-989.—Three standard soln. of bases [tributylamine in dioxan, Na methoxide in methanol - benzene and Triton B (benzyltrimethylammonium hydroxide) in pyridine] are used. Strong acids are determined by titration with one of these bases according to the other constituents of the mixture. Acyl halides are determined by reaction with ethanol followed by titration of the liberated acid with either Na methoxide or Triton B. Acid anhydrides are heated with water and pyridine and are titrated with Triton B. Reactive alkyl halides are heated under reflux with aniline, and then titrated with Na methoxide. The various mixtures of these compounds are resolved by differential titrations involving the use of all these bases, with thymol blue as indicator. Recoveries are generally $> 97\%$.

G. P. COOK

582. Application of Boldingh's technique to the chromatographic separation of some neighbouring even and odd higher aliphatic saturated monocarboxylic acids. R. Perron and A. Pourchez [Lab. de Lipochimie de C.N.R.S., Bellevue (S.-et-O.), France]. *Bull. Soc. Chim. France*, 1959, (3), 504-506.—The separation of fatty acids containing odd and even numbers of carbon atoms is described. A Boldingh chromatographic column (*Rec. Trav. Chim. Pays-Bas*, 1950, **69**, 247) is used with a stationary phase of kerosine on a slightly vulcanised rubber, and a mobile phase of water - acetone. Better separation is achieved by using a Donaldson apparatus (Donaldson *et al.*, *Anal. Chem.*, 1952, **24**, 186) for the continuous variation of the water to acetone ratio during the chromatography. Examples are given of the separation of undecanoic and dodecanoic acids, of tri- and tetra-decanoic acids, and of hexa-, hepta- and octa-decanoic acids. E. J. H. BIRCH

583. Paper-chromatographic analysis. I. Separation of α -hydroxy- α -methyl fatty acids. F. Baykut and S. Bolayir (Univ. Istanbul, Turkey). *Rev. Fac. Sci. Univ. Istanbul, Sér. C*, 1958, **23**, 77-80 (in German).—Strips (29.5 cm \times 9.8 cm) of S. & S. 2043 bM paper were treated successively with 2 N aq. acetic acid, water, 2 N aq. NH₃ and water and, after drying, were impregnated with petroleum naphtha (boiling-range 190° to 220°) (0.6 mg per sq. cm). The α -hydroxy- α -methyl fatty acids (15 μ g per 3 cu. mm) were applied at the tops of the strips, the naphtha was evaporated to 0.29 mg per sq. cm and the sample components were separated by the descending technique by the dropwise addition of 200 ml of 70% aq. acetic acid (saturated with the naphtha) over a period of 5 hr. The chromatogram was treated with copper acetate soin. (20 ml of a saturated soin. plus 80 ml of water), then washed successively with water, 2% aq. K₄Fe(CN)₆ soin. and water. The R_f values obtained after a separation time of \approx 5 hr. for 10 to 15- μ g amounts of the fatty acids of the indicated number of C atoms are given—14, 0.78; 16, 0.65; 17, 0.55; 18, 0.44; 19, 0.33; 20, 0.24.

II. Separation of the 2:4-dinitrophenylhydrazones of symmetrical dialkyl ketones. F. Baykut and S. Özeris. *Ibid.*, 1958, **23**, 86-89.—Strips of S. & S. 2043 bM paper (40 cm \times 14.5 cm) were treated with 2 N aq. NH₃, then washed twice with water and dried at 25°. The paper was then impregnated with petroleum naphtha (boiling-range 190° to 220°) (3.4 mg per sq. cm) which, after application of the sample, was evaporated to 1.7 mg per sq. cm. The strips were subjected to descending chromatography and the sample components were separated by the dropwise addition of 50 ml of 97.5% aq. acetic acid (saturated with naphtha) over a period of 10 hr. No colour development was needed for amounts $>$ 2.5 μ g. The R_f values for the 2:4-dinitrophenylhydrazones of symmetrical dialkyl ketones having the indicated number of C atoms are—21, 0.38; 23, 0.30; 25, 0.24; 27, 0.19; 29, 0.15; 31, 0.13; 33, 0.11; 35, 0.10; 37, 0.9; 39, 0.8; 41, 0.7; 43, 0.6.

CHEM. ABSTR.

584. Colorimetric determination of organic nitrates and nitramines. M. A. Laccetti, S. Semel and M. Roth (Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1049-1050.—The colorimetric FeSO₄ method was modified and extended. The stable colour produced was measured at 525 m μ and obeyed Beer's law up to 2.6 mill-equiv. of NO per mole per 100 ml of soin. Organic nitrates and

aliphatic nitramines completely liberated their N as NO, while the cyclic nitramines liberated only a fraction of it.

G. P. COOK

585. Studies on halogenosalicylaldehyde. I. Halogenosalicylaldehyde as a reagent for primary amines. Takeo Tsukamoto and Kenosuke Yuki (Pharm. Inst., Med. Fac., Kyushu Univ., Katakasu, Fukuoka). *J. Pharm. Soc. Japan*, 1958, **78** (7), 706-709.—The formation of Schiff's bases between 18 types of amines and 3-bromo-, 3:5-dibromo-, 5-chloro- and 3:5-dichloro-salicylaldehyde in ethanol has been studied. Aromatic amines give quant. yields after heating for 10 to 30 min.; aliphatic amines require heating for 2 to 3 hr. and give a yield of 50 to 60%. These reagents are suitable for the identification of sulphonamide derivatives.

K. SAITO

586. Ultra-violet spectrophotometric determination of ethylenediaminetetra-acetic acid with copper sulphate. Akira Iguchi, Yukichi Yoshino and Masuo Kojima (Coll. of Gen. Education, Tokyo Univ., Komaba, Meguro-ku). *Japan Analyst*, 1959, **8** (2), 123-126.—The copper - EDTA chelate exhibits a broad absorption band in the u.v. region at 248 m μ . in the presence of K - phthalate (I), and can be used instead of the Ni - EDTA chelate for the determination of EDTA (cf. Darbey, *Brit. Abstr. C*, 1953, 141). The extinction coeff. is proportional to the concn. of EDTA (1 to 8 \times 10⁻⁵ M) at pH 3.8 to 5.5 in the presence of CuSO₄ ($<$ 10⁻⁴ M) and I (0.001 M), and remains unchanged for 6 hr. There is no interference from $<$ 0.02 M NaCl, KCl, NH₄Cl or Na₂SO₄, $<$ 0.002 M NH₄NO₃, $<$ 0.0001 M MgCl₂ or BaCl₂, or $<$ 5% of ethanol. K. SAITO

587. Amperometric and constant-current potentiometric titration of ethylenediaminetetra-acetic acid with copper (II). W. S. Knight and R. A. Osteryoung (Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (5), 481-485.—Aq. EDTA (disodium salt) (7×10^{-3} to 7×10^{-4} M) (10 ml) can be titrated amperometrically with Cu²⁺ (\approx 0.04 M) in the presence of 0.2 M acetate buffer (50 ml) at pH 5, the rotating platinum micro-electrode being used at an applied potential of \approx 0.45 V *vs.* the S.C.E. The titration can also be made potentiometrically at pH 5 and a constant current of 1 to 5 μ A (for concn. of EDTA from 3.5×10^{-4} to 7×10^{-4} M). The accuracy is high and the standard deviation (4 to 8 determinations) is \approx 5.0%. W. J. BAKER

588. Determination of glycine in glycine - potassium trioxalatochromate(III). G. H. Spaulding (Morgan State Coll., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1109-1110.—The glycine in its complex with potassium trioxalatochromate^{III} reacts with a suspension of cupric phosphate at pH 9.1 to give cupric glycinate. The reaction mixture is centrifuged and the supernatant liquid is passed through an anion-exchange resin to remove the potassium trioxalatochromate^{III}, which interferes with the subsequent iodometric procedure. The cupric glycinate passes through the column unchanged and the copper is determined iodometrically. The results agree within 3% with those obtained by the Kjeldahl procedure. G. P. COOK

589. Determination of C₉ to C₁₀ alkylbenzenes. S. H. Hastings and D. E. Nicholson (Humble Oil and Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (11), 1924.—Infra-red data are given for *o*-, *m*- and *p*-ethyltoluene and *tert*-butylbenzene.

590. Determination of *C*₁₀ alkylbenzenes. D. E. Nicholson and S. H. Hastings (Humble Oil and Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (11), 1923.—Infra-red data are given for *o*-, *m*- and *p*-cymene.

591. Determination of butylbenzenes. S. H. Hastings and D. E. Nicholson (Humble Oil and Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (11), 1923.—Infra-red data are given.

592. Apparatus for the determination of moisture by entrainment in xylene or toluene. A. Blanzat. *Chim. Anal.*, 1959, **41** (5), 198-199.—The all-glass apparatus described and illustrated has an ascending column (insulated by a vacuum and a silvered-glass jacket) and a descending column (a condenser with a glass point to ensure that drops of H₂O fall centrally into the graduated tube). The apparatus is designed for determining H₂O in samples of coal (50 to 100 g. <2 to 3 mm size), but can be used for other substances. The reproducibility is within 2%.

W. J. BAKER

593. Detection and estimation of benzenoid compounds by chromatography. P. Moss and A. J. Thomas (Dept. of Agric. Chem., Univ. Coll. of N. Wales, Bangor). *Nature*, 1959, **183**, 1611-1612.—Methods in which chromatography and u.v. photography are used must be modified to provide light of suitable wavelength. A hydrogen discharge lamp is used as the source, and the light is filtered through a nickel sulphate-quinine sulphate soln. and a Chance OX7 filter. Details of the method are given.

H. F. W. KIRKPATRICK

594. Infra-red analysis of isomeric dicyanobenzene mixtures. N. Hadden and W. F. Hamner (Monsanto Chemical Co., Texas City, U.S.A.). *Anal. Chem.*, 1959, **31** (8), 1052-1054.—Analytical wavelengths for the determination of *o*-, *m*- and *p*-dicyanobenzene are 12.9, 12.35 and 11.8 μ , respectively. The potassium bromide disc technique is applied and a normalisation procedure eliminates the necessity for the accurate control of sample size. The results are generally accurate to about $\pm 2\%$ and reproducible to within $\pm 0.5\%$.

G. P. COOK

595. Analysis of tar acids. I. H. G. Willcock. *Chem. Age*, 1959, **81**, 831-832.—Methods for the analysis of phenols are surveyed, and include the determination of hydroxyl groups, colorimetric methods, distillation and mixed m.p. methods. In general, individual phenols in mixtures cannot be separately determined by these methods.

II. Spectroscopic and chromatographic methods. H. G. Willcock. *Ibid.*, 1959, **81**, 865.—The most rapid and reliable method for the determination of total phenols is u.v. spectroscopy. Some phenols can be identified and individually determined in simple mixtures by i.r. spectroscopy. Liquid-liquid and gas-liquid chromatography afford the best methods of separating mixtures before the determination of the components by other methods.

G. BURGER

596. Chromatographic separation of aromatic carbonyl compounds. V. L. Pikaeva (Inst. Phys. Chem., Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1959, **14** (2), 184-187.—A chromatographic method for separating and determining aromatic carbonyl compounds as their 2:4-dinitrophenylhydrazones is described. Filter-paper strips (120 to 300 mm) are passed through a 5% soln. of *n*-octanol in acetic

acid; the air-dried strips are placed in a 2-litre cylinder into which is poured 30 to 40 ml of hexane-toluene-acetic acid (6:1:3). Chromatograms are fully developed after 4 to 4.5 hr. Mixtures of benzaldehyde, phenylacetaldehyde, benzoin, deoxybenzoin and benzil were separated in this way.

K. R. C.

597. Determination of salicylic acid in the presence of benzoic and other organic acids. E. Vioque (Inst. de la Grasa, Seville). *Grasas y Aceites*, 1959, **10** (1), 35-38.—A preliminary identification of the acids is carried out chromatographically on a small silica column with bromocresol green as indicator, by comparison with a reference column. Benzoic and salicylic acids are then separated from other acids, e.g., lactic or acetic acid, by chromatography on a silica column, developing with CHCl₃. The salicylic acid is then determined colorimetrically by reaction with FeCl₃, and the benzoic acid is obtained by difference. The method has been applied to the analysis of brines of pickled olives containing anchovies, which may contain the two acids as preservatives.

L. A. O'NEILL

598. Analysis of isoctyl esters of 2:4-dichlorophenoxyacetic acid and 2:4:5-trichlorophenoxyacetic acid mixtures. F. J. Witmer, D. N. Thomas and J. B. Vernetti (Chipman Chem. Co., Portland, Ore.). *Anal. Chem.*, 1959, **31** (11), 1924.—Infra-red data are given for 2:4-, 2:5- and 3:5-dimethylbenzoyl chlorides.

599. Determination of isomeric methyl benzoyl chlorides. D. E. Nicholson (Humble Oil and Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (11), 1924.—Infra-red data are given for 2:4-, 2:5- and 3:5-dimethylbenzoyl chlorides.

600. Determination of isomeric dimethyl methyl benzoates. D. E. Nicholson (Humble Oil and Refining Co., Baytown, Tex.). *Anal. Chem.*, 1959, **31** (11), 1924.—Infra-red data are given for 2:5- and 2:4-dimethyl methyl benzoates.

601. Paper-chromatographic determination of *p*-hydroxybenzoic acid esters. H. Marx. *Rieckstoffe u. Aromen*, 1958, **8**, 293-294, 318-320.—The methods described in the literature are discussed. Several alcoholic soln. of commercially available *p*-hydroxybenzoic acid esters (**I**) were subjected to paper chromatography. Only esters were found. The chromatographic determination of **I** with acid indicators is successful only when the indicator is sensitive to the hydroxyl group. The determination of the ester by means of the diazonium salt of the sulphamic acid is best. In the isolation and determination of the esters, care must be taken to prevent saponification.

CHEM. ABSTR.

602. Chromatographic separation of thiourea and thiouracil. M. Vietti-Michelina (Inst. f. Warenkunde, Univ., Turin). *Z. anal. Chem.*, 1959, **167** (5), 352-353.—Thiourea and thiouracil may be separated by ascending or descending chromatography on Whatman No. 1 paper with one of the following solvent mixtures—*n*-butanol-acetic acid-water (5:1:4); *n*-butanol-aq. NH₃ (sp. gr. 0.88) (4:1); *n*-butanol satd. with water. *R_F* values are quoted for both ascending and descending techniques in each solvent. After developing the chromatogram for about 5 hr. (15 cm travel by the liquid front), the strip is dried and treated with ammoniacal AgNO₃ soln. The thiourea spot gives an immediate dark stain, whilst the thiouracil spot

darkens after 1 hr. Irradiation with u.v. light shows up both spots as dark patches.

T. R. ANDREW

603. Paper chromatography of 2:4-dinitrophenyl sulphide derivatives of mercaptans (thiols) and mercapto acids. E. A. Day and S. Patton (Dept. of Dairy Sci., Pennsylvania State Univ., University Park, U.S.A.). *Microchem. J.*, 1959, **3** (2), 137-141. —Methods are described for separating mixtures of the 2:4-dinitrophenyl sulphides (DNPS) of the C₁ to C₇ normal aliphatic thiols and of mixtures of mercapto acids. The preparation of DNPS derivatives of both normal thiols and some mercapto acids is described and data are presented on their m.p., light-absorption characteristics and elementary analysis. For the separation of thiols by the ascending technique, a solvent system of methanol as the stationary phase and heptane as the mobile phase was satisfactory, and examination in u.v. light at 360 m μ permitted as little as 0.03 μ g of individual components to be detected. Two procedures for the separation of the mercapto acid derivatives are described—(i) a solvent system of n-butanol - ethanol - water (4:1:5) with the water-rich layer as the stationary phase and the butanol-rich layer as the mobile phase, and (ii) benzene - 1% acetic acid (1:1), with the benzene-rich layer as the mobile phase. R_F values are given for each technique.

D. F. PHILLIPS

604. Determination of cyclohexanone and cyclohexanol in aqueous solutions. A. S. Maslennikov (Sanitation-Epidemics Sta., Gorky Region, USSR). *Zhur. Prikl. Khim.*, 1959, **32** (4), 933-934.—*Procedure for the determination of cyclohexanone (I) in the presence of cyclohexanol (II)*—To the test soln. (1 ml) containing I (1 to 100 μ g) add acetic anhydride (0.02 ml) and 10% hexamine soln. (0.2 ml), stir, add 1% Na₂S₂O₅ soln. (0.2 ml), 25% NaOH soln. (0.2 ml) and a soln. of the diazonium salt of H-acid. After 5 min. dilute to 10 ml with H₂O and measure colorimetrically. Compare with standards prepared from pure I with the same reagents. *Procedure for the determination of II in the presence of I*—Determine the concn. of I by a separate test. To the test soln. (1 ml) add 0.3 ml of a soln. of chromium trioxide in conc. H₂SO₄, stir, and set aside for 20 min.; add 10% Na₂S₂O₅ soln. (0.2 ml), a soln. of the diazonium salt of H-acid (1 ml) and stir. After 5 min. make up to 10 ml with H₂O and measure colorimetrically as before. The error of the determination of amounts >1% of either compound is \pm 10%.

K. R. C.

605. Quantitative determination of a mixture of cyclohexyl nitrite, cyclohexanone and nitrocyclohexane. B. L. Moldavskii and I. I. Ivanova (Moscow Technol. Inst. of Meat and Milk Ind.). *Zhur. Anal. Khim.*, 1959, **14** (3), 378-380.—cyclo-Hexyl nitrite (I) can be determined in the presence of cyclohexanol, nitrocyclohexane (II) and cyclohexanone (III), but II and III cannot be determined in the presence of I. *Procedure for the removal of I*—Add methanol to the test soln. (2 to 3 times the amount of I in the mixture) contained in a flask with a reflux condenser, the inner tube of which reaches to the bottom of the flask and is perforated at the lower end; CO₂ is passed (at room temp.) for 10 to 20 min. to remove I. III is determined in the flask contents by the hydroxylamine method and II alone (in alkaline soln.) by reduction with hydriodic acid. The recovery of I, II or III was \pm 97.7%.

K. R. C.

606. Ultra-violet absorption spectra of 1-nitroso-2-naphthol and its copper chelate. K. K. Chatterjee (Univ. Coll. of Sci., Calcutta, India). *Anal. Chim. Acta*, 1959, **20** (5), 423-427.—The u.v. spectra of the two compounds and of 2-naphthol in ethanol, and also of 1-nitroso-2-naphthol in 0.1 N ethanolic HClO₄, and in 0.1 N ethanolic KOH, are reported and discussed in respect of mol. structure.

W. J. BAKER

607. Paper-chromatographic separation of 1- and 2-aminoanthraquinone. A. Castiglioni (Inst. f. Warenkunde, Turin Univ., Italy). *Z. anal. Chem.*, 1959, **188** (1), 35-37.—Mixtures containing 1- and 2-aminoanthraquinone may be separated by descending paper chromatography with either benzene - glacial acetic acid (1:3) (R_F = 0.88 and 0.83 for the 1- and 2-isomers, respectively), or benzene satd. with HCl (R_F = 0.96 for the 1-isomer; the 2-isomer remains at the starting point). The process is carried out for 7 hr. in a vessel containing benzene vapour. Separation is also achieved by using an ascending technique with benzene satd. with HCl as the solvent; 1-aminoanthraquinone is then carried with the liquid front (R_F = 0.94) while the 2-isomer remains at the starting point. In both cases the mixture of isomers is applied as a soln. in 95% ethanol.

S. M. MARSH

608. Paper chromatography of indole compounds. T. Vitali and A. M. Costa Finzi (Ist. di Chim. Farm., Univ. di Parma, Italy). *Ric. Sci.*, 1959, **29** (2), 311-318.—A method of descending paper chromatography at 28° with n -propanol - 0.8 N aq. NH₃ (4:1) is described. R_F values are given of 50 indole compounds of chemical and biological importance. Four colour reactions, namely the Ehrlich, Salzkowski, nitrosation and diazo reactions, are used for locating the spots. For these reagents approximate limits of identification in μ g per sq. cm are given.

L. ZANONI

609. Colorimetric determination of 5-hydroxymethyl-2-furaldehyde in coloured glucose syrup. Yoshiro Yoshihiro and Matao Nakamura (Inst. of Ind. Sci., Tokyo Univ., Yayoi-cho, Chiba). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1959, **62** (2), 208-210.—The extraction of 5-hydroxymethyl-2-furaldehyde (I) with butanol is little affected by pH in the range 2 to 11, whereas the extinction of the aq. layer increases with increase in pH. At pH > 9.5, so small an amount of coloured substance is transferred to the butanol layer that there is no interference in the colorimetric determination of I with benzidine (cf. *Anal. Abstr.*, 1959, **6**, 1915).

K. SAITO

610. Spectrophotometric determination of D-camphor-10-sulphonic acid. F. Maggiorelli (Ist. Chim. Farm. Milit., Firenze, Italy). *Farmaco*, 1959, **14** (1), 37-43.—The method is based on the formation of the 2:4-dinitrophenylhydrazone of D-camphor-10-sulphonic acid, its dissolution in 0.1 N NaOH and extinction measurements at 268, 414 and 530 m μ .

L. ZANONI

611. Micro-separation of tetrazolium salts by paper electrophoresis. M. D. Glantz and F. Fried (Dept. of Chem., Brooklyn Coll., New York). *Microchem. J.*, 1959, **3** (2), 214-216.—A simple method is described for the separation and identification of microgram quantities of tetrazolium salts which involves electrophoresis at pH 8 to 9 for 3 hr. at 350 V. The procedure may also be useful in

ascertaining the purity of these compounds. The mobilities towards the cathode are tabulated for 11 salts.

D. F. PHILLIPS

612. Determination of alkaneethiols in hydrocarbons with silver ion and dithizone. R. K. Kunkel, J. E. Buckley and G. Gorin (Oklahoma State Univ., Stillwater, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1098-1099.—Two methods are given. In the first, the sample (0.01 to 1 mM) is titrated with Ag^+ in an ammoniacal alcoholic medium, with ammonium dithizone as indicator; the colour change at the end-point is from orange to red. The precision is within $\pm 0.2\%$. In the second, the sample (0.002 to 0.08 mM) is added to a CCl_4 soln. of silver dithizone in a spectrophotometer cell, and the extinction of the liberated dithizone is measured after 5 min. at $615 \text{ m}\mu$; the precision is $\approx \pm 2\%$. Good agreement was attained with the results from an amperometric method.

G. P. COOK

613. Colour reaction for thiosulphonates. J. F. Carson and F. F. Wong (W. Regional Res. Lab., Albany, Calif., U.S.A.). *Nature*, 1959, **183**, 1673.—For colorimetric analysis add 0.05 M N-ethylmaleimide in isopropyl alcohol (1 ml) to 0.5 to 5 μ moles of thiosulphonate [R-S(O)-SR] in isopropyl alcohol (1 ml) and then add 0.25 M KOH in the same solvent (1 ml). Measure the red or pink colour at $515 \text{ m}\mu$ at a specified time (between 10 and 18 min.) after the addition of the alkali (the colour fades rapidly for 3 min., then diminishes more slowly). The reaction enables these compounds to be distinguished from disulphides and from some thiosulphonates.

H. F. W. KIRKPATRICK

614. Elimination of preliminary depentanisation of gasoline prior to hydrocarbon-type analysis by mass spectrometry. H. E. Howard and W. C. Ferguson (Union Oil Co. of Calif., Brea, U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1048-1049.—The need for the removal of C_5 and lighter hydrocarbons can be eliminated by the use of gas-chromatographic methods in conjunction with mass-spectrometric analysis. The C_5 and lighter hydrocarbons are determined by gas chromatography, and the mass spectrum of the total petrol is corrected for their presence. No loss in accuracy is experienced.

G. P. COOK

615. Rapid determination of tetraethyl-lead in petroleum. V. Sedivec and J. Flek (Inst. Hyg. and Ind. Diseases, Prague). *Pracovni Lekarstvi*, 1958, **10** (3), 270-272.—The polarographic method of Borup and Levin (*Proc. Amer. Soc. Test. Mater.*, 1947, **47**, 1010) has been modified. *Procedure*—To 50 ml of petroleum add conc. HCl (10 ml) and shake. Heat under reflux for 30 min. Transfer to a separating-funnel, separate the aqueous layer and wash the organic layer with H_2O ($3 \times 10 \text{ ml}$); combine the aqueous layers, add gelatin soln. (0.5%) (1 ml) and dilute to 50 ml. Transfer an aliquot to the polarographic cell, remove O with a stream of N and register the wave from -0.2 to -0.7 V. Compare with a calibration curve. Samples containing from 8 to 20 mg of tetraethyl-lead per 100 ml can be determined with an error $\pm 3.5\%$. J. ZÝKA

616. Methods for the analysis and testing of coal and coke. Part 8: Chlorine in coal. British Standards Institution (2 Park Street, London, W.1). B.S. 1016: Part 8: 1959, 14 pp.—Two methods are described—(i) the Eschka method and (ii) the high

temp. method (cf. Beet and Belcher, *Fuel*, 1940, **19**, 42; Belcher and Spooner, *Ibid.*, 1955, **34**, 164; Mott and Wilkinson, *Ibid.*, 1956, **35**, 6).

617. Systematic scheme of semi-micro qualitative analysis for anionic surface-active agents. An addendum. H. Holness and W. R. Stone (Chem. Engng Dept., Manchester Coll. of Sci. and Technol., England). *Analyst*, 1959, **84**, 392.—A test omitted from among those previously reported (*Ibid.*, 1957, **82**, 166) is described. To the active material (5 mg) at the bottom of a boiling-tube is added 0.2 ml of syrupy H_2PO_4 and the tube is placed in the heating block for 10 min., the contents being maintained just below b.p. The contents are transferred into a semi-micro test-tube, diluted with an equal vol. of water, neutralised with NaOH soln. (40%), made alkaline to litmus paper with 15% Na_2CO_3 soln. and extracted with three 0.5-ml portions of light petroleum - diethyl ether (1:1). The combined extracts are washed with 50% ethanol and evaporated to a third of the initial vol. The indicator test in Table V of the scheme (*loc. cit.*) is then applied. The extracted aq. soln. is retained for subsequent tests.

A. O. JONES

618. Analytical studies on surface-active substances. I. Polyoxethylene glycols. C. J. Turi (Ist. Sup. Sanita, Rome, Italy). *R.C. Ist. Sup. Sanit.*, 1959, **22** (2), 174-188.—Polyoxethylene glycols of mol. wt. 4000 are depolymerised by heat. At 300° to 350° they are broken down to polymers of lower mol. wt., which are then further depolymerised to acetaldehyde. The breakdown can be followed by Labat's reagent (alcoholic 5% gallic acid layered over conc. H_2SO_4), which gives no colour with the higher polymers, a greenish-blue colour with polymers of mol. wt. < 600 , and a red colour with acetaldehyde. Polyoxypropylene glycols also undergo pyrolysis, yielding propionaldehyde.

L. ZANONI

619. Cloud-point as a means of characterising the polyglycols of polyoxethylene (8) stearate. M. D. Brewster and J. D. Brandner (Atlas Powder Co., Wilmington, Del., U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (5), 348-349.—The cloud-point of commercially available polyoxethylene glycol mixtures increased from 28° to 115° F with increase in the average mol. wt. from 350 to 993. The total and free polyols from polyoxethylene (8) stearate (MYRJ 45) had comparable and uniform cloud-points. The cloud-point test is sensitive to mol. wt. distribution and enables mixtures with a Poisson-type distribution of mol. wt. to be distinguished from those with the same average mol. wt. but having a non-random distribution of polyoxethylene glycols. The cloud-point test will detect the presence of 5% of material of an average mol. wt. of 600 and 1% of material of an average mol. wt. of 1000 in a polyoxethylene glycol mixture of an average mol. wt. of 340.

S. C. JOLLY

620. Complexometric determination of iron, calcium and magnesium in Turkey red oil. Z. Łada and J. Pruszyńska (Inst. of Gen. Chem., Warsaw). *Chem. Anal.*, Warsaw, 1958, **3** (5-6), 963-968.—Iron is determined directly with EDTA (disodium salt) (0.05 N), with salicylic acid or NH_4SCN as indicator, or indirectly by titration of an excess of EDTA with standard zinc soln. in the presence of Eriochrome black T. After removing the Fe by pptn. with aq. NH_3 , Ca and Mg can be determined by titration with EDTA (disodium salt).

H. DMOWSKA

621. Determination of lignin in unbleached and bleached pulps. V. Lorás and F. Leschbrant (Norwegian Pulp and Paper Res. Inst.). *Schr. Ver. Zellcheming*, 1958, 27, 225-238; *Medd. Papir-industr. Forskn. Inst., Oslo*, No. 111 (in English).—Gravimetric and absorptiometric methods are discussed and compared. The differences in the results obtained with the P.F.I. - Halse method and the C.C.A.5 method were found to be due to different amounts of acid-soluble lignin going into soln. When allowance was made for this fact by determining the lignin loss by u.v. absorption after dialysis of the filtrates, the results for "total lignin" by the two methods agreed. R. AICHER

622. Quantitative determination of synthetic fibres in papers by chemical methods. M. Faulhaber and A. Rosenberger (Bundesanstalt für Materialprüfung, Berlin-Dahlem). *Wbl. Papierfabr.*, 1958, 86, 589-594; *Paper Mkr. Lond.*, 1959, 137, 71-72, 74-75 (English trans.).—The original Marschall method in which a formic acid - zinc chloride reagent is used is applicable only to linen and rag papers. A modified method gives good results with papers containing chemical wood pulp. The shredded paper is digested with a mixture of 85% formic acid and calcium chloride (17:3, by wt.) for 45 to 60 min. at 40°, when the synthetic fibres (viscose, cuprammonium cellulose, cellulose acetate, nylon and perlon) are dissolved. If cuprammonium cellulose is present, the longer reaction time is advisable. The method gives good reproducibility. R. AICHER

623. Determination of vinyl cyanide in vinyl cyanide - vinylpyridine copolymer with concentrated phosphoric acid. Yuji Takayama and Shohei Kadota (Mitsubishi Rayon Co., Kyobashi, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1959, 62 (1), 140-142.—Vinyl cyanide (I) is decomposed with KIO_3 in conc. phosphoric acid at $<230^\circ$, whilst vinylpyridine is decomposed at $>250^\circ$ (cf. Ohashi, *Anal. Abstr.*, 1955, 2, 2448). The copolymer is fractionally decomposed in an atmosphere of CO_2 and the N is measured in nitrometer containing 40% KOH soln. The standard deviation is $\approx 0.3\%$ for 3 to 80% of I in a copolymer with 3-methyl-5-vinylpyridine. *Procedure*—Heat KIO_3 (0.3 g) in conc. phosphoric acid (5 ml), previously heated at 265°, until the evolution of gas ceases. Cool to 110°, pass a current of CO_2 , add the sample (<50 mg) and heat at 220° for 5 min.; cool to 100° and pass the gas into the nitrometer with a stream of CO_2 for 15 min. K. SAITO

624. Colorimetric differentiation of polyester- and polyether-based urethane polymers. G. F. Baumann and S. Steingiser (Mobay Chem. Co., W. Va., U.S.A.). *J. Appl. Polymer Sci.*, 1959, 1 (2), 251.—The hydroxamic acid from the urethane polyester reacts with Fe^{3+} to form a complex salt which is water-soluble and has, in most cases, an intense violet or purple colour. *Procedure*—Cut the polymer (≈ 50 mg) into small pieces, add a few drops of 2 N KOH in methanol until dark pink to phenolphthalein, followed by a few drops of satd. hydroxyammonium chloride soln. in methanol. The resulting mixture must be alkaline. With the higher cross-linked polymers, heat for 20 to 40 sec. to $>50^\circ$. After 30 to 60 sec. acidify with N HCl and add one drop of 1 to 3% aq. FeCl_3 soln. In the presence of esters the characteristic violet colour appears immediately. This test is specific for polyesters only if

no other esters are present (e.g., from solvents or plasticisers). Normally occurring functional groups in urethane polymers (e.g., urethane, urea, allophanate, biuret; amine or isocyanate groups) do not interfere. K. R. C.

625. Modified determination of polyamide end-groups. E. Turska and L. Wolfram (Politech., Łódź, Poland). *Zeszyty Nauk. Politech. Łódz. Chem.*, 1958, No. 7, 79-82.—The method of Waltz and Taylor (*Anal. Chem.*, 1947, 19, 448) is modified. A sample of polyamide (0.15 g) in benzyl alcohol (20 ml) is heated to 135° to 150° in a stream of N. The soln. is rapidly cooled to 20° (1 to 2 min.), and 3 ml of propyl alcohol is added. The soln. is stable for 20 to 25 min. and is titrated at constant temp. in the presence of phenolphthalein. Electrometric measurements were found inconvenient because of the low conductivity of the soln. Mean molecular wt. of 168 to 172 and 166 to 168 were obtained by this and by the Waltz and Taylor method, respectively. *CHEM. ABSTR.*

626. Determination of the ratio of methyl to phenyl groups in silicone polymers [by infra-red spectrometry]. J. H. Lady, G. M. Bower, R. E. Adams and F. P. Byrne (Westinghouse Res. Lab., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1100-1102.—The ratio of the methyl to phenyl groups in silicone polymers is determined by measuring the intensity of the methyl-silicon and phenyl-silicon bands at 7.92 and 6.97 μ , respectively. Reasonable agreement was reached with theoretical values and with the results obtained by another method. G. P. COOK

627. Analysis of driers. A. Zambrini. *Pitture e Verni*, 1959, 15 (1), 53-57.—A scheme for the analysis of metal driers is given. Colour, miscibility with oil, drying properties, flash-point, density, sediment and non-volatile matter are measured. The individual metals (Ca, Co, Pb, Zn and Mn) are determined, after preliminary decomposition with mineral acid, by titration with EDTA (disodium salt). L. A. O'NEILL

628. Analytical chemistry of calcium resinate. C. Norwitz (Pitman-Dunn Lab., Philadelphia, Pa.). *Off. Dig. Fed. Paint. Varn. Prod. Cl.*, 1959, 31, 441-458.—A critical review is presented of methods for the analysis and testing of technical calcium resinate. Improvements in procedure are suggested for the determination of solubility, acid value, Ca resinate content and iodine value. Ultraviolet absorption curves for Ca resinate in ethanol are given. (43 references.) D. R. DUNCAN

629. Determination of potassium persulphate in butadiene - styrene latex. M. Klátil and O. Mík (Res. Inst. Synth. Rubber, Gottwaldov, Czechoslovakia). *Chem. Průmysl*, 1959, 9 (5), 274-275.—The influence of Neokal (I) (a mixture of the butyl derivatives of naphthalene-sulphonic and -disulphonic acids) on the reduction of the persulphate ion at the dropping mercury electrode has been studied polarographically. It has been found that I deforms the persulphate wave and that, with increasing concn. of I, the front part of the wave is completely suppressed and only the rear part remains unchanged. The best wave is obtained in soln. of pH 6 to 7; no wave appears at pH <4 .

The results were used for the polarographic determination of persulphate employed as a catalyst in butadiene-styrene latex. *Procedure*—Dissolve about 10 g of the latex (measured by an injection syringe) in H_2O (20 ml) and 6*N* H_2SO_4 (2 ml) and transfer to a 100-ml flask; add methyl red soln. (5 drops), neutralise with 0.5*N* NaOH and dilute to vol. (a slight turbidity causes no interference in the polarographic determination). Remove O with N and register the polarographic wave from 1 to 1.8 V with the use of a 2-V accumulator. The method can be used for the determination of $K_2S_2O_8$ in butadiene-vinyl cyanide latex. J. ŽÝKA

630. Polarographic determination of accelerators, age-resistors and other organic substances used in the rubber industry. F. Mocker (Veith-Gummiwerke A.-G., Höchst Odenwald). *Kautsch. u. Gummi*, 1958, **11** (10), WT 281-WT 292.—The principles of the method are outlined and diagrams of the apparatus are given. The method is suitable for the rapid quant. determination of 2-mercaptopbenzothiazole (**I**) and 2-mercaptopbenzimidazole in the testing of raw materials, and in the methanol extracts of batches. The zinc salt of **I** can be determined indirectly by conversion into the corresponding acid. Provided that zinc oxide is absent, **I** can also be determined in extracts from mixtures and vulcanisates. Magnesium oxide and zinc stearate do not interfere. S. M. MARSH

631. Methods of sampling and analysis of vegetable-tanned and chrome-tanned leathers. British Standards Institution (2 Park Street, London, W.1). B.S. 1309:1959, 39 pp.—Methods for vegetable-tanned leathers include determination of volatile matter, water-soluble matter, total ash, sulphated total ash, sulphated ash of water-soluble matter, insoluble ash, oils and fats, sugars, magnesium salts, *p*-nitrophenol, pH of aq. extract and acid figure; for chrome-tanned leather additional methods are given for volatile matter, grease and uncombined sulphur, and chromium.

632. Colorimetric determination of hexahydro-1:3:5-trinitro-sym.-triazine and octahydro-1:3:5:7-tetrinitro-sym.-tetrazine in admixtures. S. Semel, M. A. Laccetti and M. R. Roth (Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1050-1052.—Both compounds when dissolved in conc. H_2SO_4 produce a red-violet colour in the presence of Fe^{2+} . Beer's law is followed at 525 $\mu\mu$ in the range 0 to 0.5 mg per ml, but the slopes of the curves differ significantly for each compound. It is therefore possible to analyse mixtures without previous separation. The mean recovery from 24 determinations was 99.94% with a standard deviation of $\pm 0.48\%$. G. P. COOK

See also Abstracts—**450**, Determination of phenylhydrazine and semicarbazide. **508**, Determination of I⁻ in petroleum brines. **741**, Identification of vegetable dyes. **773**, Trace hydrocarbons in air. **780**, Benzene in water. **788**, Cadmium anthranilate in feeding-stuffs. **800**, Apparatus for Kjeldahl digestion. **806**, Chromatography of phenols, aldehydes, ketones and carboxylic acids. **836**, Analysis of petroleum.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

633. Chemical determination of trace elements in biological materials. XVII. Fundamental studies on the conditions for dry-ashing of plant material by the use of radioactive tracers. Nobuo Suzuki (Chem. Dept., Fac. of Sci., Tohoku Univ., Kataibira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (3), 269-271.—The volatilisation of Ag from mint leaves was studied with ^{110}Ag . Below 600°, no loss was observed on heating for 10 hr. in a current of air, whilst on heating for 8 hr. at 900° about 20% of the Ag was lost. At this temp., a similar percentage of the wt. of the ash was also lost. The lost radioactivity was detected in the vicinity of the porcelain boat which contained the sample.

XVIII. Isotopic dilution analysis of silver in plant material. Nobuo Suzuki. *Ibid.*, 1959, **80** (4), 370-372.—The sample ash (≈ 1 g) from various parts of mint containing M_1 μ g of Ag is mixed with $AgNO_3$ soln. containing 0.1 to 0.2 μ g (M_2) of Ag labelled with ^{110}Ag (A_2 counts per min.) and filtered. The residue is treated with NH_4HF_2 and HNO_3 and extracted with dil. HNO_3 . The combined HNO_3 soln. is adjusted to pH 5 with ammonium citrate buffer and extracted with dithizone in CCl_4 . The organic layer is treated with 5*N* HNO_3 , adjusted to pH 5 and re-extracted, and the organic layer is treated with 5*N* HNO_3 and adjusted to give 50 ml of soln. at pH 5. The amount of Ag (M_r) is determined with dithizone and its activity (A) is measured under the same conditions as before. The amount of Ag in the sample is calculated by the formula— $A_2 = A M_r / (M_1 + M_2)$. K. SAITO

634. Internal standardisation with lithium: its use in flame photometry for biological specimens. R. E. Bernstein (Univ. Witwatersrand, Johannesburg, S. Africa). *S. Afr. J. Med. Sci.*, 1958, **23**, 103.—A comparison of various methods of internal and external standardisation indicates that replicate determinations and recoveries have smaller errors by internal standardisation, as compared with those by direct analysis in the same instrument under selected conditions. Lithium is a satisfactory internal standard for Na, and probably for K within certain concn. limits and conditions of flame operation. It is less suited to Ca, Mg and other determinations.

CHEM. ABSTR.

635. Determination of bovine serum calcium with a simple flame photometer. B. A. Dehority (Storrs Agric. Exp. Sta., Conn., U.S.A.). *J. Dairy Sci.*, 1959, **42** (5), 872-873.—Calcium is pptd. from the sample (5 ml) with water (5 ml) and 3.0% aq. ammonium oxalate soln. (2.5 ml), in a centrifuge tube. After being set aside for 20 min. the tube is centrifuged for 10 min. at 3000 r.p.m. and the residue is washed with the ammonium oxalate soln. (5 ml) followed by re-centrifugation. After dissolution of the residue in conc. HNO_3 , Li^+ are added as an internal standard and Ca (50 to 150 μ g per ml) is determined in a flame photometer. The results are discussed in relation to those given by the Clark and Collip method. W. H. C. SHAW

636. Ultra-violet spectrophotometric determination of calcium in plants with chloranilic acid. Shoji Kubo and Chuichi Tsutsumi (Food Res.

Inst., Fukagawa-Hamazono-cho, Koto-ku, Tokyo). *Japan Analyst*, 1959, **8** (2), 116-121.—Whilst the absorption in the visible region of aq. soln. of chloranilic acid (I) is markedly affected by various metals, including Al, Fe and Mg (cf. Gammon and Forbes, *Anal. Chem.*, 1949, **21**, 1391; Frost-Jones and Yardley, *Analyst*, 1952, **77**, 468), absorption in the u.v. region is only slightly affected. An isobestic point at 248 m μ provides the best wavelength for a photometric determination. The presence of <1 ml of 0.1 N acetic acid per 50 ml of the final soln. and of Mg less than the wt. of the Ca does not cause interference. The sample containing \approx 10 mg of Ca is ashed at 550°, dissolved in HCl and evaporated to dryness. The residue is extracted with 0.1 N acetic acid (20 ml), and made up to 100 ml. A 5-ml aliquot is mixed with the ammonium salt of I (0.1% soln., 5 ml), held at <15° for 3 hr., then diluted to 50 ml with water (at <15°); the Ca chloranilate is then filtered off and the extinction of the filtrate measured at 248 m μ , with I (0.1%) (5 ml) in 0.002 N acetic acid as reference soln.

K. SAITO

637. Determination of radio-strontium in biological materials. F. J. Bryant, A. Morgan and G. S. Spicer [U.K.A.E.A. (Res. Group), C.37, Royal Arsenal, Woolwich, London]. A.E.R.E. Report AERE-R 3030, 1959, 35 pp.—Procedures for the collection of materials such as soil, vegetation and bone have already been described (AERE HP/R2056); the present report includes revised methods. The separation of ^{88}Sr and ^{90}Sr from the materials is fully described; the elimination of Ca is achieved by careful control of the concn. of the HNO₃ used to precipitate the Sr and Ba in the early stages of the classical procedure. Low-background β -counting equipment is used, and details of this and the calculation procedures are given. G. J. HUNTER

638. Determination of strontium-90 in the bones of stillborn infants. E. Penna-Franca and A. P. Coelho [Inst. de Biofis., Univ. do Brasil, Rio de Janeiro]. *An. Acad. Brasil. Cienc.*, 1959, **31** (1), 49-52.—Calcium is first determined by standard methods. The sample is suitably cleaned, ashed and dissolved in conc. HCl. Ca²⁺ and Sr²⁺ are pptd. as phosphates and separated by the solubility of the nitrates in 75% HNO₃. Yttrium carrier is then added, and the equilibrium between ^{90}Sr and ^{90}Y is attained in 2 weeks. The yttrium oxalate is then pptd. and counted by means of a Geiger-Müller tube. A modified procedure is described, in which Fe(OH)₃ is used for the preliminary removal of radioactive impurities.

C. A. BLAU
W. R. O'NEILL

639. Rapid method for the determination of phosphorus, nitrogen, magnesium, calcium, sodium and potassium in faeces and diets. R. Santini and J. M. de Jesus (U.S. Army Tropical Res. Med. Lab., Fort Brooke, Puerto Rico). *Amer. J. Clin. Path.*, 1959, **31** (2), 181-187.—Weighed aliquots of diluted homogenised faeces or diets are heated with H₂SO₄, and H₂O₂ is added at intervals until a clear digest is obtained. Ions interfering with the determination of Ca, K and Na are removed by passing the digested samples through a column of an anion-exchange resin. The various elements are determined by known methods. The results obtained by this rapid procedure agree closely with those obtained by digesting with HNO₃·HClO₄ and by the macro-Kjeldahl method. P. NICHOLLS

640. Complexometric determination of sulphates in urine. J. Čajda (KHES, Dept. Hyg., Martin, Czechoslovakia). *Pracovní Lékařství*, 1958, **10** (6), 530-531.—*Procedure*—Mix the sample of urine (5 ml) with dil. HCl (4 ml), transfer to a centrifuge tube and heat for 20 to 30 min. on a water bath. Cool, add H₂O (20 ml) and, drop-wise, 5% BaCl₂ soln. (2 ml); set aside for 12 hr., add acetone (3 drops) and separate the ppt. in the centrifuge. Remove the supernatant liquid, wash the residue with H₂O (10 ml), add acetone and repeat the centrifuging and washing. To the residual ppt. add 0.02 M EDTA (disodium salt) (10 ml), H₂O (10 ml) and NH₄Cl - aq. NH₃ buffer soln. (pH 8 to 10) (5 ml), and mix. When dissolution of the ppt. is complete (2 hr.) and Eriochrome black T as indicator and titrate with 0.02 M MgCl₂ to a red-violet end-point.

J. ČAJDA

641. Determination of iron(III) by using sodium 4-aminosalicylate. H. Łukasiak-Wardzińska and J. Popowicz (Chem. Dept., Med. Acad., Białystok, Poland). *Chem. Anal., Warsaw*, 1958, **3** (5-6), 893-895.—Iron (1 to 15 μg in 10 ml) is determined colorimetrically in alkaline soln. The intensity of the colour is proportional to the concn. of Fe and is measured in a Fulfrič photometer against a reagent blank, with a 5-cm cell and S42 filter. Copper and Zn in concn. normally found in blood serum do not interfere.

H. DMOWSKA

642. Direct determination of drug concentrations in biological fluids by polarography. P. O. Kane (Res. Lab., May and Baker Ltd., Dagenham, Essex, England). *Nature*, 1959, **183**, 1674.—Degassed normal sera from rats, rabbits, horses and humans showed no polarographic waves in the range -0.1 to -1.1 V. It is suggested that drugs giving well-defined waves within this region can be determined directly without the need for any extra supporting electrolyte or buffering. Experiments with 2-ethyl-4-thioureidopyridine (I) showed that it could be readily determined when added to serum. In urine the range is reduced to -0.2 to -0.7 V and acidification is necessary to bring the wave of I within this range.

H. W. F. KIRKPATRICK

643. Quantitative estimation of isonicotinic acid hydrazide [isoniazid] and 4-aminosalicylic acid in blood serum. H. C. Leifheit and E. R. B. Smith (Dept. of Chem., Walter Reed Army Inst. of Res., Washington, D.C.). *Amer. J. Clin. Path.*, 1960, **31** (2), 142-147.—Isoniazid (I) is extracted into an organic solvent and re-extracted into acid. Free I is determined as a coloured complex with 4-hydroxy-3-methoxybenzaldehyde, and total I (free I plus acetyl I) is determined as a complex with *p*-dimethylaminobenzaldehyde (II) after acid hydrolysis. 4-Aminosalicylic acid is extracted into the same organic solvent, but is re-extracted with alkali and determined as a complex with II. As serum often contains non-specific chromogens that react as I under the conditions of the determination, it is necessary to carry out control determinations on patients before therapy. P. NICHOLLS

644. Determination of pyrazinamide. VI. Studies on the separatory determination of pyrazinamide, isoniazid and other metabolites in urine. Hitoshi Sezaki (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1958, **78** (11), 1211-1215.—Pyrazinamide (I), pyrazinoic acid (II), acetylated isoniazid (III) and isonicotinic acid

(IV), together with isoniazid (V) and its metabolites (VI), are adsorbed on, and fractionally eluted from, a column of Amberlite IRA-40 (cf. Sezaki, *Ibid.*, 1956, **76**, 906), which retains all the named compounds. *Procedure*—(i) **I**, **III**, **V** and **VI** are eluted with water (200 ml). An aliquot is treated with bromine water (to convert **V** and **VI** into **IV**) and passed through a column of activated alumina, which retains most of the **IV** and some interfering substances. An aliquot of the percolate is treated with sodium nitroprusside and NaOH, and the extinction is measured at 494 m μ to give **I** + **IV**; a second aliquot is treated with Na₂CO₃ and BrCN, and measured at 425 m μ to give **IV** alone. (ii) A second aliquot from the resin column is treated with H₂SO₄ and K₂Cr₂O₇ (to convert all metabolites of **V**, except **III**, into **IV**). It is then passed through an alumina column, which retains **IV** and Cr₂O₇²⁻, and an aliquot of the percolate is treated with bromine water followed by NaNO₃ to convert **III** into **IV**, which is then measured at 425 m μ after treatment with Na₂CO₃ and BrCN. (iii) After elution of **I**, **III**, **V** and **VI** as described above, the resin column is eluted with 10% NaCl soln. (50 ml) which desorbs **II** and **IV**. An aliquot of the eluate is acidified with acetic acid and passed through a column of alumina, which retains **IV**. The column is washed with 1% NaCl soln. and **II** is eluted with N NaOH and determined at 477 m μ after treatment with sodium nitroprusside at 40°. **IV** in a second aliquot is determined at 425 m μ as described above.

VII. Determination of 4-pyrazinamidosalicylic acid and 1-pyrazinoyl-2-isonicotinoylhydrazine and related compounds. Hitoshi Sezaki, *Ibid.*, 1958, **78** (11), 1215-1219.—4-Pyrazinamidosalicylic acid (**VII**) in urine is determined by de-proteinising the sample with Pb acetate, removing the excess with NaH₂PO₄ and centrifuging. The supernatant liquid is passed through an alumina column, which is washed with water, Na acetate soln. and water again. **VII** is then eluted with N NaOH, the eluate is treated with sodium nitroprusside at 40°, and the extinction is measured at 480 m μ . For the determination of 1-pyrazinoyl-2-isonicotinoylhydrazine (**VIII**), the urine is treated with H₂SO₄ and K₂Cr₂O₇, and passed through a column of alumina. **VIII** is eluted from the column with water and the eluate is treated with bromine water followed by NaNO₃ soln. and passed through a second alumina column. The column is washed with water, and **IV** is eluted with 10% NaCl soln. and determined colorimetrically at 425 m μ as described above. K. SAITO

645. Determination of meprobamate in urine. Applicability to other compounds containing an NH group. G. H. Ellis and C. A. Hetzel (Wyeth Inst. for Med. Res., Radnor, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1090-1091.—The compound is treated at room temp. with a hypochlorite soln. at pH 10.5 to form the N-chloro derivative. The excess of hypochlorite is decomposed by phenol in dil. HCl and the derivative is treated with an excess of KI. The iodine formed is measured colorimetrically, either as KI₂ or as the starch-iodine blue complex, at 350 or 625 m μ , respectively. The concn. range is about 10 to 30 μ g. The method was applied to the determination of meprobamate (after previous extraction with ether) in urine. The mean recovery from urine was 82.1%, with a coeff. of variation of $\pm 1.05\%$. G. P. COOK

646. Amperometric determination of sulphydryl [mercapto] content of blood and tissues. S. K. Bhattacharya (Dept. of Biochem., Univ., Leeds).

Nature, 1959, **183**, 1327.—The mercapto group is determined by amperometric titration with 0.002 M AgNO₃ in tri(hydroxymethyl)methylamine buffer, at pH 7.4. For total mercapto-group determinations, tissue homogenates (1 to 2 ml) and haemolysed blood samples (0.1 ml haemolysed with 1 ml of de-ionised distilled H₂O) are used, whilst sulphosalicylic acid extracts (1 to 5 ml of sample extracted with 2.5% soln. of acid and then neutralised with 0.8 M NaHCO₃) are used for the non-protein mercapto-group determinations. A blank titration is performed after the mercapto groups have been blocked with *p*-chloromercuribenzoate. The apparatus is assembled as described by Benesch *et al.* (*J. Biol. Chem.*, 1955, **216**, 663), except for the platinum electrode, which is formed from four twisted pieces of wire, bent laterally into a U-shape. J. H. WATON

647. Quantitative determination of some carbohydrates [xylose, arabinose, glucose, galactose, lactose] in normal urine. J. W. Date (Inst. of Hygiene and Biochem., Univ. of Aarhus, Denmark). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (2), 153-162.—Urine specimens (24 hr.) are collected under toluene and are stored at -20° until required. Aliquots of 5 to 13 ml are used, depending on the sp. gr. and original volume, and these are treated by the previously described method (*Ibid.*, 1958, **10**, 149), modified in that 20 times the aliquot volume is collected from the de-ionising column. The concentrated urine (25 to 125 μ l) is chromatographed on Whatman No. 1 paper by a descending two-dimensional method, with the upper layer of *n*-butanol - pyridine - benzene - water (5:3:1:3) for the first dimension, and *n*-butanol - acetic acid - H₂O (4:1:5) for 48 hr., or ethyl acetate - acetic acid - H₂O (3:1:3) for 72 hr., for the second dimension. For detection and determination of the separated sugars, the previously described method (*loc. cit.*) is used, and methods for the identification of the isolated compounds are given. Recoveries of 92% to 102% are obtained by this method.

D. B. PALMER

648. Paper-chromatographic detection of D-galactose in urine. G. Zinner (Inst. f. Pharm. Chem., Univ. Marburg/Lahn, Germany). *Dtsch. ApothZtg.*, 1959, **99** (21), 481.—The use of the "wick" procedure (ascending paper chromatography in which the solvent is continuously evaporated) (Pfeil *et al.*, *Angew. Chem.*, 1958, **70**, 702) enables D-galactose (0.2%) to be detected in urine (0.003 ml) in the presence of glucose. In 15 to 20 hr. galactose rises 8 to 12 cm and glucose 2 to 3 cm more; fructose moves more rapidly still. Aniline phthalate in butanol is used as the locating agent on the dried paper, and 0.5% glucose soln. is run for comparison on the same paper. J. P. STERN

649. The paper chromatography of chloroplast pigments. Z. Šesták (Inst. Plant Physiol., Biol. Fac., Charles' Univ., Prague). *Czechos. Biol.*, 1958, **7** (2), 153-159.—*Procedure*—The filtered acetone extract is transferred into purified light petroleum, evaporated to a small vol. and chromatographed by the descending technique on Whatman No. 1 paper impregnated with a 2% soln. of sucrose. The separation is carried out in darkness at 5° with the use of the following solvent systems—benzene - light petroleum - acetone (10:2.5:2), hexane - *n*-propanol (99.5:0.5), light petroleum - CHCl₃ - *n*-propanol (3:1:0.01), light petroleum -

benzene - CHCl_3 - isopropyl alcohol (80:5:5; 1) or light petroleum - benzene - n -propanol (94:5:1).

J. ŽÝKA

650. Determination of some short-chain dicarboxylic acids in urine by paper chromatography. K. Stalder (Max-Planck-Ges., Göttingen, Germany). *Hoppe-Seyl. Z.*, 1958, **311**, 221-226.—A method is presented for the determination of malonic, methylmalonic and succinic acids in urine. The acidified urine is extracted with diethyl ether and this extract is further extracted with light petroleum. The light petroleum extract is separated by paper chromatography with the consecutive use of the solvent systems ethanol - ammonium carbonate buffer (6:2) and isoamyl formate - water - formic acid (11:1:2). A semi-quant. evaluation is possible by taking into account the relation between size of spot and log of concn. Determinations were carried out on rat and human urines, and tests were made in which known amounts of these acids were added to urine samples; 60 to 80% can be recovered by this method.

CHEM. ABSTR.

651. Organic analysis. IX. Modified method for the determination of glucuronic acid with 1:3-dihydroxynaphthalene. Tsutomu Momose, Yo Ueda, Masako Yoshinaga, Junko Masui and Michiko Nagasaki (Pharm. Inst., Med. Fac., Kyushu Univ., Katakasu, Fukuoka). *J. Pharm. Soc. Japan*, 1958, **78** (9), 1064-1066.—The method of Fishman and Green (*Anal. Abstr.*, 1956, **3**, 478) has been examined and some modifications are proposed. The extinction increases with increase in acid concn. (optimum, 2 N) and the time of heating (optimum, 1 hr.). The intensity of the colour due to glucose increases with time, but the molar extinction coeff. is < 1 that of glucuronic acid. Urine and blood are deproteinised with Na_2WO_4 (10%) and H_2SO_4 (0.66 N), then diluted 20-fold, and a 2-ml portion is heated with 1:3-dihydroxynaphthalene soln. (0.2% 2 ml) and 6 N HCl (2 ml) in a boiling-water bath for 1 hr., and cooled in ice water for 10 min. The product is mixed with saturated NaCl soln. (5 ml), and shaken with benzyl alcohol (6 ml); the organic layer is separated and filtered, and the extinction is measured at 615 $\text{m}\mu$.

K. SAITO

652. Determination of 4-hydroxy-3-methoxymandelic acid in urine by high-voltage paper electrophoresis. W. von Studnitz and A. Hansson (Dept. of Clin. Chem., General Hospital, Malmö, Sweden). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (1), 101-105.—Urine (1 ml) is brought to pH 1.0 by addition of HCl, 1 ml of satd. NaCl soln. is added, and the phenolic acids are extracted with ethyl acetate (2 x 4 ml). The combined extracts are evaporated to dryness at 40° in an air current, and the dry residue is dissolved in 0.2 ml of abs. ethanol. For the electrophoresis, a current of 100 mA (2000 V) is applied, resulting in a potential gradient of 55 V per cm. A buffer (pH 6.0) of pyridine - acetic acid - water (10:1:89, by vol.) is used, and the separation takes 3 hr., during which time the 4-hydroxy-3-methoxymandelic acid (I) migrates 15 cm from the cathode. The papers are dried at 80° for 30 min., and are then sprayed with a diazo reagent consisting of a mixture of 0.1 g of *p*-nitroaniline in 2 ml of conc. HCl, made up to 100 ml with water, 0.2% aq. NaNO_2 soln., and 10% aq. K_2CO_3 soln. (1:1:2, by vol.). Each soln. is stored at 4°, and the spray is prepared just before use. On drying the paper in a current of cold air the I

is revealed as a blue-violet spot; the other phenolic acids present produce red or yellow spots. For a quant. determination, a series of known volumes of I soln. (120 μg per ml in 10% ethanol) is run alongside a known volume of the urine extract, and the paper is sprayed as described above. The coloured spots are then eluted with methanol - 2% aq. Na_2CO_3 soln. (2:1, by vol.) (4 ml) and the extinctions of the eluates are determined at 520 $\text{m}\mu$, against a paper blank. A standard curve is prepared from the values given by the pure substance, and the unknown concn. is obtained from it. Beer's law is obeyed for a range of 0.0 μg to 3.0 μg of I. This method is claimed to be less time-consuming and simpler than previously described procedures.

D. B. PALMER

653. The photometric determination of phenylpyruvic acid in urine. A. Saifer and A. F. Harris (Isaac Albert Res. Inst., Jewish Chronic Dis. Hosp., Brooklyn, N.Y., U.S.A.). *Clin. Chem.*, 1959, **5** (3), 203-217.—The addition of Fe^{2+} and a reduced temp. are employed to stabilise the FeCl_3 reaction. *Procedure*—To 1.0 ml of urine add 4.0 ml of glycine buffer (pH 2.2) (4.35 g of glycine and 3.40 g of NaCl are dissolved in H_2O , 420 ml of 0.1 N HCl is added and the vol. is made up to 1 litre) and 1.0 ml of uranyl nitrate reagent [4% of $\text{UO}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the glycine buffer]. Place in an ice bath for 10 min. and centrifuge at 3000 r.p.m. for 5 min. To 5.0 ml of the supernatant liquid add 1.0 ml of an ice-cooled 9.8% soln. of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ in the glycine buffer and 0.1 ml of cooled 10% aq. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ soln. Mix, set aside in the ice bath in the dark for 30 min. and read the colour at 630 $\text{m}\mu$. Read standards containing 25, 50 and 75 mg of Na phenylpyruvate per 100 ml and a urine blank similarly.

H. F. W. KIRKPATRICK

654. Polarographic determination of gentisic acid in biological material. M. Jirka (II Inst. Med. Chem., Charles' Univ., Prague). *Cas. Lek. Čes.*, 1958, **97** (6-7), 237-239.—A specific polarographic method is described for the determination of gentisic acid (I) ($\approx 100 \mu\text{g}$ per ml) in serum and urine during gentisic or salicylate therapy. Chlorides interfere in the determination of I in serum. *Procedure*—Mix the sample (3 ml) with 7 N H_2SO_4 (1 ml) and extract by shaking for 1 min. with diethyl ether (10 ml) and centrifuging. Transfer the ether extract (5 ml) to a separating-funnel, extract I into a carbonate buffer soln. (pH 8.7) (5 ml) and register the anodic wave of I.

J. ŽÝKA

655. Use of butyl acetate in determination of sialic acids. T. Miettinen and I.-T. Takki-Luukkainen (Dept. of Med. Chem., Univ., Helsinki, Finland). *Acta Chem. Scand.*, 1959, **13** (4), 856-858.—In the resorcinol - hydrochloric acid reaction for the determination of sialic acids (*cf.* Svennerholm, *Anal. Abstr.*, 1958, **5**, 198), butyl acetate containing approx. 15% of butyl alcohol is a better extractant than amyl alcohol; it separates rapidly without centrifuging, even in the presence of proteins, and extracts less of the pigments formed by other carbohydrates.

W. T. CARTER

656. Analysis of pharmaceuticals by the indophenol reaction. V. Determination of hesperidin and eriodictin in citrin. Konosuke Murai (Hospital Pharmacy, Nara Med. Coll., Shijo-cho, Kashihara, Nara-ken). *J. Pharm. Soc. Japan*, 1958, **78** (7), 745-748.—Both hesperidin (I) and eriodictin (II)

give almost identical absorptions (max. 620 m μ) by the indophenol reaction. Their hydrolysed products are separated by paper chromatography with water satd. with benzene as developer (K_F = 0.44 for I, 0.11 for II). The sample (citrin, 50 mg) is heated with 5% HCl in ethanol (20 ml) on a water bath, and the product is neutralised and made up to 50 ml with pyridine (10 ml) and water. An aliquot (0.5 ml) is chromatographed, the two spots are cut out, extracted with 20% aq. pyridine soln. (5 ml) for 30 min. on a boiling-water bath, filtered off and washed with aq. pyridine to make the total vol. 10 ml. A 2-ml aliquot is mixed with phosphate-borate buffer (pH 8.2), dimethyl-*p*-phenylenediamine (0.05%, 0.5 ml) and NaClO soln. (0.02%, 0.3 ml) and shaken with isobutyl alcohol (4 ml). A 3.5-ml aliquot of the organic layer is mixed with ethanol (0.2 ml) and the absorption is measured at 620 m μ .

K. SAITO

657. Ultra-violet fluorescence of quinine sulphate for detection of phosphate ester spots on paper. E. S. Rorem (W. Utilization Res. and Devel. Div., Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif.). *Nature*, 1959, **183**, 1739-1740.—Immerse the developed and dried paper in a 0.5% soln. of quinine sulphate dihydrate (I) in abs. ethanol, dry at room temp. for a few minutes and examine under u.v. light in a darkened room. The spots show as light areas against an intense grey-blue fluorescent background. As little as 0.007 μ mole of P can be detected. Purines, pyrimidines and nucleosides and relatively high concn. of free sugars and amino acids also give the test. After marking the spots, I can be washed from the paper with abs. ethanol, and the spots eluted, or submitted to other detection procedures.

A. R. ROGERS

658. Determination of unesterified fatty acids in blood and tissues. R. Dzúrik, P. Kovács and T. R. Niederland (III Med. Univ.-klinik, Bratislava, Czechoslovakia). *Naturwissenschaften*, 1959, **46** (9), 327.—The method is based on that of Dole (*J. Clin. Invest.*, 1956, **35**, 150). *Procedure*—Homogenise the sample (one part) with CHCl_3 -methanol (2:1) (20 parts) and filter. Shake an aliquot of the filtrate, containing 0.001 milli-equiv. of unesterified fatty acid, with one-fifth of its vol. of H_2O , centrifuge, discard the aq. phase, rinse the apparatus with H_2O and again discard the aq. phase. Evaporate to dryness in an atmosphere of N and titrate with 0.002 N NaOH under N to thymol blue. The filter-paper should be purified by extraction with ethanol for 24 hr. in a Soxhlet apparatus.

A. R. ROGERS

659. Colorimetric method for the determination of micro amounts of higher unesterified fatty acids (C₁₂ to C₁₈) in blood. D. Mendelsohn (Univ. Witwatersrand, Johannesburg, S. Africa). *S. Afr. J. Med. Sci.*, 1958, **23**, 75-82.—Blood is oxalated. Plasma is acidified with H_2SO_4 , methylal-methanol (4:1, v/v) is added, and the tube shaken. Methanol and light petroleum are then added, with mixing, until the solvents form a single phase; water is added and the system separates into two phases. More light petroleum is added and the mixture is stirred. The tube is centrifuged, and most of the clear upper light-petroleum phase is transferred to another container. The extraction is repeated, and the extracts are combined and evaporated to dryness. The residue is dissolved in isopropyl alcohol and rosaniline reagent is added.

The mixture is heated at 46° for 30 min., then cooled, and benzene is added. A reagent blank is prepared from isopropyl alcohol and rosaniline reagent treated similarly. The colour is read in an Evelyn photo-electric colorimeter, with a 520-m μ filter. The concn. of unesterified fatty acids is calculated from a calibration curve prepared with stearic acid. The results expressed in milli-equiv. per litre are calculated on the assumption that the average mol. wt. of the higher unesterified fatty acids in blood is 280. Blood samples were taken from 20 fasting volunteers, aged from 15 to 28 years, and the plasma contained 0.107 to 0.410 milli-equiv. of unesterified fatty acids per litre.

CHEM. ABSTR.

660. Determination of hexosamines (in tissue).

L. Bolognani, G. Coppi and V. Zambotti (Ist. Chim. Biol., Univ. di Pavia, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1958, **34** (23-24), 1950-1951.—*Procedure*—The tissue homogenate is passed through a Dowex column (H^+ form) (200 to 400 mesh). The interfering substances are removed with H_2O and the hexosamine is eluted with 10 ml of 2 N HCl. The eluate is dried over KOH, then acetylated, and the colour is developed with a modified Ehrlich reagent (2.67 g of *p*-dimethylaminobenzaldehyde in 80 ml of abs. ethanol and 20 ml of conc. HCl). This colour has a max. extinction at 530 m μ and obeys the Beer-Lambert law. By this method it is possible to determine from 5 to 90 μ g of hexosamine.

L. ZANONI

661. Applications of nitrometry. XVII. Determination of glucosamine.

Makoto Yokoo (Res. Lab., Takeda Pharmaceutical Ind. Ltd., Osaka, Japan). *Chem. Pharm. Bull. Japan*, 1959, **7** (1), 23-26 (in English).—Amino sugars are determined in the hydrolysis products of heparin and chondroitinsulphuric acid, which also contain amino acids, by determining the total amino-N nitrometrically with HNO_2 (Yamagishi and Yokoo, *J. Pharm. Soc. Japan*, 1954, **74**, 278). The N other than in glucosamine is then determined nitrometrically after heating the hydrolysed sample soln. for 20 min. at 100° in soln. with acetylacetone soln. (2% by vol. in 0.5 N Na_2CO_3). Under these conditions $\geq 400 \mu\text{g}$ of glucosamine is converted into a pyrrole deriv. which does not react with HNO_2 to give N. Hydrolysis of the polysaccharides is effected by heating for 5 hr. in a sealed tube in 4 N HCl at 100°. Results of determinations on heparin are tabulated.

E. J. H. BIRCH

662. Determination of catecholamines in blood.

M. P. Keenan, W. P. Kleitsch and F. L. Humoller (Med. Res. Lab., V.A. Hosp., Omaha, Neb., U.S.A.). *Clin. Chem.*, 1959, **5** (3), 239-247.—The amines are adsorbed on alumina and eluted with 0.2 M acetic acid. They are then coupled with ethylenediamine and the compounds are extracted with butanol; the fluorescence is measured at 510 m μ , with 436 m μ as the exciting wavelength; precautions are taken during these operations to exclude light. The butanol is then exposed to a "daylight" bulb for 30 min. and the residual fluorescence is measured. The readings given by known mixtures of adrenaline (I) and noradrenaline (II) before and after exposure to light are used to calculate the amounts present in the unknown sample. Exposure to light scarcely affects the fluorescence of the I derivative, but reduces that of the II complex to a very low level.

H. F. W. KIRKPATRICK

663. Determination of serotonin (5-hydroxytryptamine) in human blood. T. P. Waalkes (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (5), 824-829.—After the pptn. of blood proteins, serotonin is extracted from alkaline soln. into ethyl acetate or *n*-butanol and is then purified and concentrated on columns of cellulose treated with succinic anhydride or by re-extraction into acid, respectively. The fluorescence of the resulting soln. is then measured on a spectrofluorimeter at 540 m μ with activating radiation of 300 m μ . Results on normal blood ranged from 0.09 to 0.18 μ g per ml; those on abnormal samples are given and discussed.

W. H. C. SHAW

664. Isolation and identification of the products of the oxidation of choline. [Determination of betaine aldehyde.] M. Jellinek, D. R. Strength and S. A. Thayer (Dept. of Biochem., St. Louis Univ. Sch. of Med., Mo., U.S.A.). *J. Biol. Chem.*, 1959, **234** (5), 1171-1173.—The deproteinised soln. or reaction mixture which contains 10 to 100 μ g of betaine aldehyde is mixed with a satd. soln. (1 ml) of 2:4-dinitrophenylhydrazine in *N* HCl. The soln. is diluted to 5 ml and heated in a boiling-water bath for 5 min., then cooled to room temp.; 2 *N* NaOH (10 ml) is added, the soln. is diluted to 50 ml, and the extinction is measured at 438 m μ . The amount of aldehyde is then ascertained from a standard graph.

J. N. ASHLEY

665. Polarographic determination of urocanic acid. E. Krejčí, M. Kútová, J. Král, A. Ženíšek and J. Stolz (II Inst. of Med. Chem., Charles' Univ., Prague). *Cas. Lék. Čes.*, 1958, **97** (27-28), 857-861.—Urocanic acid (**I**), an important intermediate product of histidine metabolism, yields a well-developed polarographic wave in acetate buffer soln. of pH 4.7, suitable for analytical purposes and for the determination of **I** in human sweat. *Procedure*—Mix equal vol. of the sweat sample and of acetate buffer soln. (pH 4.7), remove O with a stream of N and register the polarographic wave from -1.0 V. In the range from -1.30 to -1.35 V, the wave corresponds to **I**, and a second wave corresponds to an unknown compound. In other types of biological material **I** can be determined polarographically after a previous chromatographic separation on Whatman No. 1 paper with *n*-butanol - acetic acid - H_2O (4:1:5) and elution of the separated **I** with boiling H_2O . For samples containing \approx 6 mg of **I** per 100 ml an accuracy within \pm 2% was achieved.

J. ZÝKA

666. Application of a new paper-chromatographic micro elution technique to the isolation and identification of guanine nucleotides from pigeon erythrocytes. E. Gerlach and H. Fikentscher (Physiol. Inst., Univ., Freiburg i. Br., Germany). *Naturwissenschaften*, 1959, **46** (9), 326-327.—Guanosine triphosphate (**I**) is separated from guanosine diphosphate and adenine nucleotides by the paper-chromatographic procedure of Gerlach *et al.* (*Pflügers Arch.*, 1957, **263**, 682). The desired bands are cut out and eluted separately by a technique which permits the collection of the eluate (30 to 40 μ l) in a graduated capillary tube. Five tests are given which serve to confirm the identity of **I**.

A. R. ROGERS

667. Quantitative determination of deoxyribonucleic acid in cells by Feulgen micro-spectrophotometry. C. Leuchtenberger (W. Reserve Univ., Cleveland, Ohio). *Gen. Cytochem. Methods*, 1958,

1. 219-278.—The procedure consists of three main steps—(i) preparation of the biological material, (ii) application of the Feulgen reaction on slides and (iii) micro-spectrophotometric measurement at 546 m μ of the complex of Feulgen dye and deoxyribonucleic acid contained in the individual nuclei. With minor modifications, the Feulgen procedure is that described by Stowell (*Stain Technol.*, 1945, **20**, 45). When the results are compared with those of biochemical analyses good agreement is obtained whenever tissues with a uniform cell population are examined.

K. R. C.

668. Bromocresol purple as an aid in the location of amino acids on descending paper chromatograms. R. H. Mandl (Boyce Thompson Inst. for Plant Res., Yonkers, N.Y.). *Contr. Boyce Thompson Inst.*, 1958, **19** (5), 461.—Bromocresol purple is suitable as a marker for amino-acid chromatography since it moves \approx 10% faster than the leucines in the six solvent mixtures tested.

N. E.

669. Purification of plant amino-acids for paper chromatography. J. F. Thompson, C. J. Morris and R. K. Gering (U.S. Dept. of Agric., Ithaca, N.Y.). *Anal. Chem.*, 1959, **31** (6), 1028-1031.—Basic amino acids are retained on the ammonium form of Dowex-50 resin, and other amino acids are held on the hydrogen form. All the amino acids are eluted with aq. NH₃ and the hydrolysis of labile substances is avoided by carrying out the procedures at $<6^\circ$. Recoveries are generally $>97\%$ for the purification of about 20 amino acids in the pure form and from protein hydrolysates and plant extracts.

G. P. COOK

670. Determination of amino acids from plants by paper chromatography. J. F. Thompson and C. J. Morris (U.S. Dept. of Agric., Ithaca, N.Y.). *Anal. Chem.*, 1959, **31** (6), 1031-1037.—Three procedures are described. Neutral and acidic amino acids are separated by two-directional chromatography, leucine, isoleucine and phenylalanine by one-directional chromatography, and basic amino acids by one-directional chromatography. All the spots are located with ninhydrin, and after elution are determined colorimetrically at 570 m μ . The coeff. of variation is less than 5% in the concn. range from 10 to 80 μ g; approx. 20 acids were determined. Good agreement was reached with the results obtained by other methods in the analysis of a β -lactoglobulin sample.

G. P. COOK

671. Analysis of mixtures of amino acids by gas-phase chromatography. C. G. Youngs (Prairie Reg. Lab., Nat. Res. Council of Canada, Saskatoon, Sask.). *Anal. Chem.*, 1959, **31** (6), 1019-1021.—The amino acids are converted into their N-acetyl butyl esters which are then fractionated on a firebrick column coated with a hydrogenated vegetable oil. Glycine, alanine, valine, leucine, isoleucine and proline are quant. determined in synthetic mixtures and in protein hydrolysates. The maximum deviation is \pm 10%.

G. P. COOK

672. The determination of proline and hydroxyproline. A. Iachan, R. Roitman and J. C. Perrone (Inst. Nacional de Tecnol., Rio de Janeiro). *An. Acad. Brasil. Cienc.*, 1959, **31** (1), 53-55 (in English).—Amino acids are selectively destroyed with HNO₃ (Hamilton and Ortiz, *J. Biol. Chem.*, 1950, **187**, 733). Unattacked proline (**I**) and hydroxyproline (**II**) are separated by paper chromatography and

converted by spraying with ethanolic-fluoro-2:4-dinitrobenzene into their dinitrophenyl derivatives, which are extracted by the method of Isherwood and Cruickshank (cf. *Anal. Abstr.*, 1954, 1, 2771) and measured spectrophotometrically at 385 $\mu\mu$ for I and 380 $\mu\mu$ for II. The Beer-Lambert law holds for concn. $< 25 \mu\text{g}$. C. A. BLAU
W. R. O'NEILL

673. Paper chromatography of dinitrophenyl-amino acids. G. Biserte, J. W. Holleman, J. Holleman-Debove and P. Sautière (Biochem. Lab., Fac. of Med. and Pharm., Lille, France). *J. Chromatography*, 1959, 2 (3), 225-271 (in French).—A detailed review is given of the application of paper chromatography to the identification and determination of dinitrophenyl(DNP)-amino acids. Sections deal with the preparation of specific derivatives, the dinitrophenylation of a protein hydrolysate, a protein and a peptide, the paper chromatography of ether-soluble and water-soluble DNP-amino acids, and of DNP-peptides. The quant. chromatography of the derivatives is considered in the final section. (95 references.)

S. M. MARSH

674. System for separating sulphur and non-sulphur amino compounds by two-dimensional paper chromatography. D. Margolis and R. H. Mandel (Boyce Thompson Inst. for Plant Res., Yonkers, N.Y.). *Contr. Boyce Thompson Inst.*, 1958, 19 (6), 509-512.—Data obtained by separating 25 sulphur compounds, 12 maleimide adjuncts of mercapto compounds and 39 non-sulphur-containing amino acids, amides and amines with a two-dimensional descending paper-chromatographic system are presented. The development in the first direction is with ethanol-*tert*-butyl alcohol-58% (w/v) aq. NH_3 -water (12:4:1:3). The second solvent is *tert*-butyl alcohol-88% (w/v) formic acid-water (14:3:3). The locating reagents are platinic iodide, 0.05 M N-ethylmaleimide and ninhydrin. N. E.

675. Electrophoretic control of salt separation of blood serum proteins. R. A. Gudovich and Z. S. Sukhareva. *Akad. Nauk UzSSR*, 1958, 309-312; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (17), Abstr. No. 22,099.—The serum is diluted (1:5) with H_2O , and K_2HPO_4 (0.21 g) is added at 30° to a 1-ml aliquot. After 10 min. the ppt. is removed and two further fractions are ppts. by the addition of 0.35 g and 0.47 g of K_2HPO_4 per ml of soln., respectively. Paper electrophoresis in borate buffer at pH 8.6, μ 0.125, shows that γ -globulin is brought down with the first ppts. and α - and β -globulins with the second. The γ -globulin obtained by electrophoresis in borate buffer at pH 8.6 is separated into two fractions, but in barbitone buffer at pH 8.6 it is homogeneous. Albumin remaining in soln. after the second ppts. is homogeneous after electrophoresis in borate or barbitone buffer at pH 8.6, but is separated into two fractions with a borate-phosphate buffer. K. R. C.

676. Dipotassium hydrogen phosphate for the separation of serum proteins. Z. I. Sukhareva. *Akad. Nauk UzSSR*, 1958, 375-380; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (17), Abstr. No. 22,135.—Normal blood serum was diluted (1:5) with normal saline, K_2HPO_4 soln. (6 ml) was added at various concn. to the dilute serum (0.6 ml) and the ppts. protein determined turbidimetrically. The protein was completely ppts. with 2.6 M K_2HPO_4 , γ -globulin was ppts. with 1.09 to 1.11 M K_2HPO_4 .

β -globulin with 1.17 to 1.24 M, α_1 -globulin with 1.3 to 1.56 M and α_2 -globulin with 1.35 to 1.72 M K_2HPO_4 . The results are reproducible and in good agreement with those obtained by paper electrophoresis.

K. R. C.

677. Studies on the serum proteins. IV. The dye-binding of purified serum proteins separated by continuous-flow electrophoresis. F. W. Sunderman, jun., and F. W. Sunderman (Div. of Metab. Res., Jefferson Med. Coll., Philadelphia, Pa., U.S.A.). *Clin. Chem.*, 1959, 5 (3), 171-185.—Purified fractions were used in tests with bromophenol blue and Amido black 10B (C.I. Acid Black 1). Dye-binding is not a strictly linear function of protein concn., especially when the concn. is low ($< 40 \mu\text{g}$). In the protein concn. range 40 to 80 μg the affinities of the globulins for Amido black 10B averaged about 80%, and for bromophenol blue about 60%, of that of the albumin. H. F. W. KIRKPATRICK

678. Use of nigrosine for dyeing proteins in electrophoresis on filter-paper. M. Ortega (Fac. Farm., C.S.I.C., Madrid). *An. Real Acad. Farm.*, 1958, 24, 15-35.—A new method for dyeing protein fractions of human serum is described. Water-sol. nigrosine in 1% acetic acid was used as the dye, and optimum conditions for coloration were determined. A study was made with normal sera, and average values were obtained for the relative percentages of albumin and α_1 , α_2 , β - and γ -globulins. A study was made of normal serum values and umbilical-cord blood-serum values obtained with nigrosine dyeing techniques. The results were compared with methods in which Amido black 10B (C.I. Acid Black 1), bromophenol blue and Light green (C.I. Acid Green 5) were used. A classification was possible by comparing the behaviour of the sera dyed with nigrosine and with other dyes. A new component of prealbumin was noted, the clinical significance of which has not been disclosed. CHEM. ABSTR.

679. Comparison of plasma protein fractions by the Kjeldahl and biuret methods and refractive index measurements. W. Knouse and J. I. Routh (State Univ., Iowa City, U.S.A.). *Proc. Iowa Acad. Sci.*, 1958, 65, 241-245.—Pooled human serum was fractionated and the composition of the fractions determined electrophoretically. The Kjeldahl and biuret methods were applied to the fractions and refractive index measurements were made. The values obtained by each method were linear with respect to the protein concn. When compared at a given concn., values obtained by the three methods did not agree, but appeared to differ on the basis of the amounts of lipid and the percentage of N present in each fraction. CHEM. ABSTR.

680. Staining of glycoproteins on electropherograms. A. A. Titaev and E. G. Larskil (Inst. Paediatrics, Acad. Med. Sci., Moscow). *Lab. Delo*, 1959, 5 (3), 25-31.—*Procedure*—Prepare the protein electropherograms in the usual way, fix the filter-paper strips at 100° to 200°, immerse them for 10 min. in acetone, then dry them in air. Immerse the strips in 3% methanolic KIO_4 soln. for 45 min., rinse ($\times 3$) with H_2O , place them first in an acid fuchsin soln. for 10 min., then in 0.8% aq. $\text{K}_2\text{S}_2\text{O}_8$ soln. to which conc. HCl has been added just before use (12 ml of HCl per litre of soln.) and shake gently for some seconds. Rinse the strips a few times with fresh soln., immerse for 10 min. in acetone and air-dry. The glycoproteins are revealed as red-violet bands; the paper is also coloured but bleaches

rapidly. Measure the length of each band and section the strip. Place each cm-section in a test-tube with 0.5 N NaOH (10 ml) in a boiling-water bath for 15 min., cool and add glacial acetic acid (1 ml); add *n*-butanol (5 ml), stopper the tube, shake gently and set aside for a day, or centrifuge for immediate measurement. Remove the coloured *n*-butanol layer and measure its extinction at 550 m μ against *n*-butanol. In the range of 0.005 to 0.08 ml of blood serum the colour intensity of the electropherogram increases in direct proportion to the amount of blood serum, *viz.*, the glycoprotein content; above 0.08 ml the linear relationship no longer holds.

K. R. C.

681. Determination of lipoproteins [in blood serum] by means of paper electrophoresis. R. Ya. Výsotskii and E. G. Livshits (Riga Med. Inst., USSR). *Lab. Delo*, 1959, 5 (3), 31-34.—The blood sample was centrifuged for 5 min. at ≥ 2500 r.p.m. The best separation was obtained with an aq. barbitone-barbitone sodium buffer (barbitone sodium 8.76 g, barbitone 1.38 g per litre) at pH 8.6 and ionic strength 0.05. Blood serum (0.06 to 0.08 ml) was placed on uniformly moistened filter-paper strips and the current (140 to 150 V, 0.12 mA per cm) applied immediately. The separation took 15 to 18 hr. The strips were dried at 50° to 80° or at room temp. Sudan black B was the most effective stain, the colour being allowed to develop for 6 hr. The electropherograms were washed in 50% ethanol, and the fractions were revealed as blue zones of different shades on a white background. The relative proportions were determined either by elution or by direct photometric measurement. Phospholipoproteins can be determined on the same electropherogram after photometric measurement of the lipoproteins, which are eluted in pure acetone baths until the acetone is colourless. In healthy individuals α -phospholipoproteins amount to $45 \pm 10\%$ of the total in blood serum, β - to $40 \pm 15\%$, and γ - to $15 \pm 10\%$. K. R. C.

682. Determination of the haptoglobin group. C.-B. Laurell (Dept. Clin. Chem., Univ. of Lund, Sweden). *Scand. J. Clin. Lab. Invest.*, 1959, 11 (1), 18-19.—A method is described for sera containing low concn. of haptoglobin. Haemoglobin is added to such sera in excess of the haemoglobin-binding capacity, and an electrophoretic separation is performed with a gel prepared by boiling starch with a phosphate buffer (pH 7.5, 0.0067 M). A weak phosphate buffer (0.03 M) is used for the electrophoresis bridges and vessels. The free haemoglobin migrates towards the cathode, producing a clear separation of the haptoglobin groups, which migrate towards the anode. A s.c.n. of benzidine (sadt.), acetic acid (10%) and hydrogen peroxide (0.2%) is used to develop the electrophoretic pattern. D. B. PALMER

683. Determination of haemoglobin in plasma by near-ultra-violet spectrophotometry. M. Harboe (Central Lab., Univ. Hosp., Rikshospitalet, Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1959, 11 (1), 66-70.—The method is based on the absorption of soln. of oxyhaemoglobin (I) at 415 m μ , *i.e.*, in the Soret band. Blood samples, obtained by venepuncture, are collected in one-tenth of the total volume of 3.1% aq. Na citrate soln., in apparatus treated with silicone to prevent "induced haemolysis." The samples are centrifuged immediately for 10 min. at 600 g and +4°, and only the top half of the separated plasma is used for the

determination. The plasma (1 ml) is diluted with 10 ml of 0.01% Na₂CO₃ soln. [for soln. containing < 5 mg of haemoglobin (II) per 100 ml use a dilution of 1:6], and the extinction is measured at 380 m μ , 415 m μ and 450 m μ , with 1-cm cells and 0.01% Na₂CO₃ soln. as the blank. The concn. of I is calculated from the formula of Rimington and Sveinsson (*J. Clin. Lab. Invest.*, 1950, 2, 209), which eliminates the natural absorption of plasma or serum and also that due to turbidity. I soln. is prepared from the red cells of defibrinated blood from a non-smoker, which are well washed with saline soln., haemolysed by alternate thawing and freezing and adjusted to a concn. of I of $\leq 1\%$ by the addition of water. To determine the II content of this soln. it is diluted (1:200) with 0.01% Na₂CO₃ soln. and the extinction is measured at 543 m μ . The identification of the pigment measured and the influence of derivatives of II are discussed. This method is simple, each analysis taking only 5 min., and it can be applied to other media containing II, but not to icteric plasmas or sera. D. B. PALMER

684. The determination of sulphohaemoglobin in blood. V. Holeček (Inst. Hyg. and Ind. Diseases, Prague). *Pracovní Lékařství*, 1958, 10 (4), 348-353.—Two methods are recommended. The first is based on the determination of the difference of the extinctions at 617 and 650 m μ of dil. soln. of haemolysed blood satd. with CO and treated with dithionite. The second is based on the determination of the extinctions at 620 and 650 m μ of dil. soln. of haemolysed blood after the addition of KCN.

J. ZÝKA

685. The determination of saponins in Japanese plants belonging to the *Dioscoreace*. I. Colorimetric determination of diosgenin and tokorogenin. Masaharu Tamagishi and Iiso Nakamura (Res. Lab., Takeda Pharm. Ind., Juso-nishino-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1958, 78 (9), 1068-1072.—Diosgenin and tokorogenin give an orange-red (max. absorption, 500 m μ) and a purple (560 m μ) colour with SbCl₃ in nitrobenzene and in phenol, respectively. The former changes its intensity with the time of heating, but becomes almost constant after heating for 10 to 30 min. at 60°, and becomes more intense on the addition of aq. methanol; tokorogenin is inactive towards the nitrobenzene reagent.

K. SAITO

686. Paper chromatography of steroids in systems with ethanediol as the stationary phase. L. Stárka and M. Prusíková (Res. Inst. of Endocrinology, Prague, Czechoslovakia). *J. Chromatography*, 1959, 2 (3), 304-307.—Steroids in CHCl₃ soln. are applied to Whatman No. 1 paper and the strip is then soaked in 30% ethanediol (I) in methanol. The chromatograms are developed in a tank saturated with the vapours of the mobile phase by using a descending technique at 17° to 20°. The mobile phases used are toluene saturated with I for corticosteroids, and light petroleum (boiling-range 45° to 65°) for 17-oxosteroids. *R_f* values of some corticosteroids and 17-oxosteroids in the respective systems are tabulated, and the effect of the I concn. on the *R_f* values of some 17-oxosteroids is shown graphically. The main advantages of I are that a high velocity of partition is obtained, it is readily available in a grade of satisfactory purity, and it does not interfere with most of the colour reactions used for the determination of steroids in urine. The method has been applied to the separation of corticosteroids

and 17-oxosteroids from biological material, particularly from urine extracts, as well as for the separation of pure steroids. S. M. MARSH

687. Ultra-violet spectrophotometric method for the determination of cholesterol. B. I. Weigensberg and G. C. McMillan (Dept. of Path., Path. Inst., McGill Univ., Montreal, Canada). *Amer. J. Clin. Path.*, 1959, **31** (1), 16-25.—The method is based on the absorption in the 204 to 206- μ region by the ethylene link in the B ring of cholesterol (I). I is extracted from serum and plasma with an acetone-ethanol mixture and from arterial tissue with diethyl ether. Free I is pptd. by the addition of digitonin and total I is pptd. by this reagent after saponification. The ppt. is dissolved in methanol and the spectrum is measured from 200 to 220 μ . This method is three times as sensitive as the usual colorimetric procedures, and is not markedly influenced by variables such as time, temp., light, moisture and concn. of reagents. P. NICHOLLS

688. Characterisation of unsaturated steroids by their absorption spectra in the far ultra-violet. K. Stich, G. Rötzler and T. Reichstein (Org.-chem. Anst., Univ. Basel, Switzerland). *Helv. Chim. Acta*, 1959, **42** (5), 1480-1502.—By the technique described, steroids have been identified, substituents recognised, and, in most cases, the degree of substitution determined. The position of the double bond cannot yet be determined. The Beckman DK-2 spectrophotometer used was chosen specially for good scattered light properties. By using a correction for scattered-light, ϵ values down to 185 μ in cyclohexane and 195 μ in ethanol have been determined. Values for 44 compounds are listed. E. G. CUMMINS

689. Fluorescence spectra of oestrogens, and the selection of primary and secondary filters. Fumio Akasu and Hiroshi Ohki (Toho Univ. Med. School, Japan). *Japan. J. Endocrinol.*, 1958, **34**, 740-744.—A method is presented for the determination of oestrone (I), oestradiol (II) and oestriol (III) in urine. When I, II and III are extracted, separated by alumina column chromatography (Napp and Kersten, *Arch. Gynäkol.*, 1957, **188**, 279) and treated with 90% H_2SO_4 for 20 min. at 80°, they give absorption peaks at 450, 455 and 455 μ , respectively. With the same H_2SO_4 treatment the standard I, II and III soln. give peaks at 450, 430 and 450 μ . The fluorescence of I, II and III is greatest at 430 μ , and spectra produced at this wavelength have max. at 485, 490 and 485 μ , respectively; max. for the standard I, II and III soln. are found at 485, 480 and 485 μ , respectively. The apparatus consists of a V₁ filter (max. transmittance at 436 μ) as the primary filter and a filter transmitting light above 450 μ plus an interference filter passing a narrow range at \approx 485 μ (for I and III) or 490 μ (for II) as the secondary filter. The method gives the minimum blank fluorescence, and is not influenced by other urinary substances excreted in pregnancy urine after multiple-vitamin administration. CHEM. ABSTR.

690. Simplified physico-chemical method for determination of human urinary oestrogens. T. El-Attar (Donner Lab. of Biophys. and Med. Phys., Univ. of California, Berkeley, U.S.A.). *Nature*, 1959, **183**, 1607.—Enzymatic hydrolysis with β -glucuronidase is followed by extraction with diethyl ether and separation of the phenolic steroids. The oestrogen

extract is purified by counter-current distribution and the oestrogens are determined fluorimetrically by the reaction with H_2SO_4 . H. F. W. KIRKPATRICK

691. Paper-chromatographic separation and quantitative colorimetric determination of 17-oxosteroids in urine. P. Göbel, F. Heni and A. d'Addabo (Univ. Klin. Tübingen, Germany). *Hoppe-Seyl. Z.*, 1958, **311**, 201-212.—Urine is hydrolysed either with HCl on a boiling-water bath or with β -glucuronidase in acetate buffer (pH 5), followed by treatment with H_2SO_4 at room temp. The soln. is extracted with diethyl ether and the extract is treated with a satd. soln. of Na_2CO_3 followed by 10% NaOH soln.; it is washed with water (pH 7) and evaporated to dryness. The keto fraction is separated by means of Girard reagent T and the content of 17-oxosteroids is determined. The 17-oxosteroids (600 to 700 μ g) are dissolved in dichloromethane-propane-1:2-diol (20:1) and applied to paper strips. The descending technique is used. Propane-1:2-diol-acetone (1:4) is used as the stationary phase and methylcyclohexane as mobile phase. The strips are developed for 6 to 21 hr., dried, drawn through an alkaline m-dinitrobenzene soln. [a 2% soln. of m-dinitrobenzene in abs. ethanol-30% KOH (3:2)], dried again for 10 min. at 40°, and measured colorimetrically. The separation and quant. determinations of androsterone, *æ*etiocholanolone, hydro*æ*piandrosterone, 11-oxoandrosterone, 11-oxo-*æ*etiocholanolone, 11-hydroxyandrosterone and 11-hydroxy*æ*etiocholanolone are described. Androsterone cannot be separated from *æ*pietiocholanolone, nor can *æ*etiocholanolone be separated from *æ*piandrosterone. CHEM. ABSTR.

692. Fluorimetric measurement of rat-plasma and adrenal corticosterone concentration. R. Guillemin, G. W. Clayton, H. S. Lipscomb and J. D. Smith (Baylor Univ. Coll. Med., Houston, Tex., U.S.A.). *J. Lab. Clin. Med.*, 1959, **53** (5), 830-832.—Details are given of the routine use of the method of Silber *et al.* (*Clin. Chem.*, 1958, **4**, 278) with the minor modifications introduced for the assay of plasma (0.5 to 2.0 ml) and of adrenal corticosteroid concn. in rats. W. H. C. SHAW

693. Polarographic reduction of non-conjugated steroid ketones. P. Kabasakalian and J. McGlotten (Schering Corp., Bloomfield, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1091-1094.—The direct polarographic reduction of non-conjugated ketones in various positions on the nucleus and the side-chain of a steroid molecule is described. The reduction of hydroxyl and acetoxy groups, alpha to a carbonyl group, is reported. The reduction wave of these groups in 20-oxosteroids merged with the reduction wave of the carbonyl group. Two distinct waves were obtained with 16-hydroxy (or acetoxy)-17-oxosteroids. The experiments were carried out in 90% ethanol, with tetrabutylammonium chloride as the base electrolyte. G. P. COOK

694. Determination of peroxidase in tobacco. A. Ollero Gómez and A. Panque Guerrero (Inst. de Biología del Tabaco, Seville). *Bol. Inst. Nac. Invest. Agron., Madrid*, 1959, **19** (40), 1-21.—Methods available for the determination of peroxidase are reviewed. The preferred methods for

application to tobacco are those of Balls and Hale (*J. Ass. Off. Agric. Chem.*, 1933, **16**, 445) and Purr (*Biochem. Z.*, 1950, **321**, 1). The method of Purr is the more suitable in cases of low peroxidase activity. Working details and results obtained by both methods are reported.

E. C. APLING

695. Biosynthesis of β -hydroxy- β -methylglutaryl coenzyme A in yeast. I. Identification and purification [and assay] of the hydroxymethylglutaryl coenzyme-condensing enzyme. J. J. Ferguson, jun., and H. Rudney (Dept. of Biochem., Western Reserve Univ., Cleveland, Ohio, U.S.A.). *J. Biol. Chem.*, 1959, **234** (5), 1072-1075.—The condensing-enzyme activity is assayed optically by measurement of the decrease of acetoacetyl coenzyme A (**I**) in the presence of acetyl coenzyme A (**II**) (which condense to give β -hydroxy- β -methylglutaryl coenzyme A). The assay depends on the absorption of the enolate ion of acetoacetyl thiol esters in alkaline soln., and is based on a standard assay for acetoacetyl thiolase, the extinction being determined spectrophotometrically at 310 m μ . The difference in the rates of decrease of absorbance before and after addition of **II** is considered to be due to the condensation of the two coenzymes. Dilute soln. of the enzyme are stabilised by the addition of albumin, and Mg²⁺ are added to make the assay more sensitive by increasing the apparent extinction coeff. of **I** at 310 m μ . The presence of (NH₄)₂SO₄ or PO₄³⁻ does not affect the assay. With purified enzyme preparations there is a linear relation over a fivefold range of enzyme concn.

J. N. ASHLEY

696. Fluorimetric method for measuring the activity in serum of glutamic-oxalacetic transaminase. T. Laursen and G. Espersen (Dept. Clin. Chem., Rigshospitalet, Copenhagen, Denmark). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (1), 61-65.—This method depends on the determination of di-phosphopyridine nucleotide (**I**), which is condensed with ethyl methyl ketone to produce a compound having a strong stable fluorescence in alkaline soln. Serum (0.2 ml) is incubated with a substrate consisting of nicotinamide, reduced **I**, malic dehydrogenase, ketoglutarate and aspartate, for 10 min. at 37°. The reaction is stopped by the addition of trichloroacetic acid, and **I** produced is condensed with ethyl methyl ketone, the resulting fluorescence being determined with a soln. of quinine sulphate as standard. A standard curve is prepared to cover a range of 0.0 to 0.25 μ mole of **I**. The influence of various factors (e.g., substrate concn., amount of serum, incubation time, temperature and pH) is reported.

D. B. PALMER

697. Purification [and determination] of neuraminidase from *Vibrio cholerae*. G. Schramm and E. Mohr (Max-Planck-Inst. f. Virusforsch., Tübingen, Germany). *Nature*, 1959, **183**, 1677-1678.—A method of determination for control during the purification of the enzyme is described. Mucoprotein from human urine prepared by a modification of the method of Tamm and Horsfall (*J. Exp. Med.*, 1952, **95**, 71) was used as a standard. Urinary mucin (4 mg) containing 3.8 to 4.1% of neuraminic acid is dissolved in 1 ml of H₂O, the enzyme soln. (0.001 to 0.2 ml) is added, and the total vol. is made up to 2 ml with 0.1 M acetate buffer (pH 5.5). After incubating for 15 min. at 37°, 2 ml of satd. soln. of benzoic acid in CHCl₃ is added to stop the reaction, the tube is shaken vigorously and centri-

fuged at 3500 r.p.m. for 4 min. Neuraminic acid is determined on 1 ml of the clear supernatant liquid by the orcin method of Böhm *et al.* (*Anal. Abstr.*, 1954, **1**, 2755). Each μ g of neuraminic acid liberated under these conditions is taken as 1 unit of specific activity (E). The purity of the enzyme is measured by the value of E per μ g of protein N in the preparation.

H. F. W. KIRKPATRICK

698. Theory of agar diffusion methods for bioassay. R. K. Finn (Cornell Univ., Ithaca, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 975-977.—Agar diffusion methods are reviewed, together with the theory of linear diffusion of an antibiotic. (23 references.)

G. P. COOK

699. Microbiological assay of amino acids, vitamins and antibiotics. Application of tube methods. H. W. Loy and W. W. Wright (U.S. Dept. of Health, Education and Welfare, Washington, D.C.). *Anal. Chem.*, 1959, **31** (6), 971-974.—A review of the analytical procedural details involved in microbiological tube assays is presented. The care and attention required for the maintenance of the test organism and the preparation of the medium and the sample material are emphasised. (29 references.)

G. P. COOK

See also Abstracts—337, Use of enzymes in analysis. **571.** Determination of hexoses. **572.** Detection of glucose, fructose and mannose. **717.** Separation of corticosteroids. **727.** Meprobamate in urine. **799.** Apparatus for breath analysis. **801.** Apparatus for dialysis. **821, 823.** Protein electrophoresis. **832.** Titration of deuterohaematin.

Pharmaceutical analysis

700. Influence of spectral slit width on the absorption of visible or ultra-violet light by pharmaceutical substances. A. R. Rogers (Sch. of Pharm., Brighton Tech. Coll., Sussex, England). *J. Pharm. Pharmacol.*, 1959, **11** (5), 291-296.—The importance of narrow slits in the spectrophotometric determination of extinction coefficients has been demonstrated. Care is needed in the B.P. 1958 spectrophotometric tests or assays of apomorphine hydrochloride, chloroquine phosphate and sulphate, diiodohydroxyquinoline, naphazoline nitrate, papaverine hydrochloride and especially procyclidine hydrochloride to avoid spuriously low results.

A. R. ROGERS

701. Micro-estimation of opium alkaloids in pharmaceuticals by paper chromatography. K. Genest and C. G. Farmilo (Food and Drug Directorate, Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (5), 286-289.—Subject a mixture which contains morphine, codeine, thebaine and papaverine to descending chromatography on Whatman No. 1 paper impregnated with (NH₄)₂SO₄, with isobutyl alcohol-acetic acid-H₂O (50:5:12) as solvent. After development for 16 hr., dry the chromatogram and spray it with potassium iodoplatinate soln. Evaluate by the use of a self-integrating densitometer which enables 5 to 50 μ g of the alkaloids to be quant. analysed with a coeff. of variation of about $\pm 4\%$. The method has been applied to the analysis of nine pharmaceutical preparations with satisfactory results.

A. R. ROGERS

702. **Determination of morphine in opium.** C. A. Teygeler (Rijksinst. v. Pharmacotherapeutisch Onderzoek, Leiden, Netherlands). *Pharm. Weekbl.*, 1959, **94** (7), 201-209.—In an investigation of the Ned. P. VI method, in which the opium extract is purified by passage through alumina followed by the pptn. of morphine by 1-chloro-2:4-dinitrobenzene, errors were found to be due to the adsorption of morphine on the alumina and the co-pptn. of codeine. The pptn. time prescribed (6 hr.) is insufficient, and should be increased to 24 hr.

M. J. MAURICE

703. **Assay of reserpine.** E. Kahane and M. Kahane (Fac. des Sci., Montpellier, France). *Ann. Pharm. Franç.*, 1958, **16** (12), 726-737.—The micro-Ziesel method for the determination of reserpine is not suitable for dil. soln. The fluorescence and u.v. absorption of soln. have been investigated. The fluorescence of reserpine is accompanied by decomposition and the appearance of a yellow colour, and it is shown that fresh soln. of reserpine do not fluoresce, but that the fluorescence develops under the influence of u.v. light. The u.v. absorption in CHCl_3 gives a max. at 268 $\text{m}\mu$ and a step at 295 $\text{m}\mu$, and the ratio of the extinctions at the max. and the step is 1.83 ± 0.05 . The absorption at 268 $\text{m}\mu$ follows Beer's law. Aged soln. show a change in the ratio. The products of decomposition are removed by passing the soln. through a column of "Hyflo Super-Cel" cellulose, which does not retain the reserpine. Dioxan, methanol and acetic acid can also be used as solvents, methanol being considered the best. Concn. of 20 μg per ml are used.

E. J. H. BIRCH

704. **Spectrophotometric determination of nicotine.** K. Eschle (Reaktor A.-G., Würenlingen, Aargau, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (4), 258-263.—Standard curves for pure nicotine, tobacco "nicotine" and tobacco-smoke "nicotine" are given. They were determined by measuring the maximum of the u.v. extinction with a Beckman spectrophotometer model DU. In contrast to the work of Swain *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 1341) and Willits *et al.* (*Anal. Chem.*, 1950, **22**, 430), considerable differences between the three groups were found. Interfering substances such as pyridine probably account for these discrepancies. For each individual group the standard curve was surprisingly reliable. The results obtained from a large variety of tobaccos, pure and mixed, fermented and unfermented, do not deviate more than 5% from the values of the standard curve.

I. DICKINSON

705. **Photometric determination of nicotine in tobacco and tobacco smoke.** P. Waltz, M. Häusermann and E. Nyari (Vereinigten Tabakfabriken A.-G., Neuchâtel-Serrières). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (3), 159-165.—The method described is based on that of Wartmann and Harlow (133rd National Meeting of the Amer. Chem. Soc., San Francisco, 1958). Nicotine in tobacco is steam-distilled in the presence of NaCl and NaOH into N HCl (15 ml) (soln. A). A 5-ml portion is diluted to 25 ml with 0.05 N HCl (soln. B). Extinctions C_1 (at 236 $\text{m}\mu$) and C_2 (at 282 $\text{m}\mu$) are measured on soln. A and C_3 (at 259 $\text{m}\mu$) on soln. B. Then the nicotine (%) in the tobacco = $3856/P[C_2 - (C_1 + C_3)/10]$, where P = wt. (mg) of tobacco taken. The nicotine in smoke is absorbed in CHCl_3 , then extracted with 0.1 N H_2SO_4 ; an aliquot is steam-

distilled after the addition of NaOH and the nicotine determined as described above.

G. BURGER

706. **Titration of total alkaloids in *Tabernanthe iboga* roots.** G. Ghielmetti and C. Mela (Lab. Ric. Fitochim. "Inverni & Della Beffa" Milano, Italy). *Farmaco*, 1959, **14** (1), 32-36.—Procedure—The powdered sample (2 g) is moistened with 2 ml of 10% Na_2CO_3 soln. and mixed with 3 g of Celite. After 2 hr. the mixture is placed in a chromatographic column, and eluted with CHCl_3 , collecting 200 to 250 ml of eluate; this is washed with H_2O in a separating-funnel, dried with anhyd. Na_2SO_4 and evaporated to dryness. The residue is dissolved in acetic acid and titrated with 0.1 N HClO_4 in acetic acid soln. in the presence of crystal violet as indicator (0.5% in acetic acid soln.), or potentiometrically.

707. **Solubility of antibiotics in twenty-four solvents. II.** M. L. Andrew and P. J. Weiss (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (5), 277-279.—The solubilities tabulated include those of 16 further salts of the antibiotics studied previously (Weiss *et al.*, *Ibid.*, 1957, **7**, 374) and 22 salts of 14 new antibiotics.

W. H. C. SHAW

708. **Dose-response lines for antibiotic microbial assays.** A. Kirshbaum, B. Arret and S. D. Harrison (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (5), 301-306.—Statistical procedures are applied to the specific requirements for determining the rectilinear portions of the dose-response curves of microbiological assays. The methods are applied to turbidimetric assays for bacitracin, chloramphenicol, dihydrostreptomycin, oleandomycin, penicillin and tetracycline.

W. H. C. SHAW

709. **Control of mixtures of antibiotics by electrophoresis on paper.** P. Castel, R. Mus and J. Storck (Fac. de Pharm. de Montpellier, France). *Ann. Pharm. Franç.*, 1959, **17** (1), 63-71.—The following antibiotics (with their mobilities relative to streptomycin) are detected by electrophoresis on paper (Arches No. 301) in a buffer consisting of pyridine 6 ml, acetic acid 20 ml and water to 1 litre, with a p.d. of 225 V—penicillin G (-0.38), Extencillin (benzathine penicillin) (-0.30), oxytetracycline (+0.16), chlortetracycline (+0.16), tetracycline (+0.20), bacitracin (+0.38), carbomycin (+0.40), erythromycin (+0.47), oleandomycin (+0.51), spiramycin (+0.76), quinine penicillin (+0.76), procaine penicillin (+0.76), D-cycloserine (+0.79), viomycin (+0.91), streptomycin (+1.00), framycetin (+1.34) and neomycin (+1.36). Reagents for detecting the compounds on the paper are described together with the application of the procedure to known mixtures.

E. J. H. BIRCH

710. **Photometric determination of streptomycin and dihydrostreptomycin.** E. M. Barilaro and M. Katz (Cátedra de Quím. Biol., Univ. Tucumán). *An. Asoc. Quím. Argentina*, 1958, **48** (4), 310-317.—The method is based on measurements of the reducing power with Folin and Wu's reagents.

E. C. APLING

711. **Metal chelate compounds of tetracycline derivatives. VIII. Colorimetric determination of tetracycline with boric and sulphuric acids.** Keiji Sekiguchi (Pharm. Inst., Med. Fac., Hokkaido Univ., Sapporo). *J. Pharm. Soc. Japan*, 1958, **78**

(9), 965-969.—The colorimetric method of Sakaguchi for the determination of chlortetracycline with H_3BO_3 in conc. H_2SO_4 (cf. *Anal. Abstr.*, 1956, **3**, 520) is applied to the determination of tetracycline (I) (5 to 35 μ g per ml). The max. absorption shifts towards the violet with increase in concn. of H_2SO_4 , the molar extinction coeff. gradually increasing to reach a constant value in H_2SO_4 of concn. $> 83.5\%$. Interference results from NO_2^- and NO_3^- . I is separated with an anion-exchange resin (e.g., Dowex 2) by the usual method. The sample soln. (1 ml) is mixed with H_3BO_3 in conc. H_2SO_4 (1% w/v, 9 ml), and the extinction is measured after 1 hr. at 500 $m\mu$. The coeff. of variation is $< \pm 5\%$.

K. SAITO

712. Spectrophotometric assay for chlortetracycline hydrochloride and tetracycline hydrochloride in pharmaceuticals. F. S. Chiccarelli, M. H. Woolford, jun., and M. E. Avery (Lederle Lab. Div., American Cyanamid Co., Pearl River, N.Y.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (5), 263-268.—The method of Chiccarelli *et al.* (cf. *Anal. Abstr.*, 1958, **5**, 1013) has been applied to the determination of chlortetracycline in a number of pharmaceutical preparations. To determine tetracycline in these preparations, prepare an aq. soln. which contains about 200 μ g per ml. To one 5-ml aliquot add 10% $NaHSO_3$ soln. (1 ml) and phosphate buffer (pH 7.5) (10 ml), heat in a bath of boiling water for 3 min., add 5 N HCl (6 ml), heat for 5 min., then cool and dilute with H_2O to 50 ml; heat another 5-ml aliquot (as blank) with $NaHSO_3$ soln. (1 ml) and buffer (pH 7.5) (10 ml) for 3 min., then cool, add 5 N HCl (6 ml) and dilute with H_2O to 50 ml. Measure the extinctions of the two soln. at 434 $m\mu$.

A. R. ROGERS

713. Determination of glycyrrhizic acid in liquorice. Hidehiko Hada and Mizuho Inagaki (Res. Lab., Morishita Jintan Co., 543, Tamahori-cho, Higashi-ku, Osaka). *J. Pharm. Soc. Japan*, 1958, **78** (7), 795-797.—Glycyrrhizic acid (I) gives a max. absorption at 252 $m\mu$ in 40 to 60% (v/v) ethanol and at 258 $m\mu$ in 0.03 to 0.1 N aq. NH_3 , the extinction being proportional to the concn. in the range from 10 to 100 μ g per ml. Glycyrrhetic acid (II), also present in liquorice, gives a similar absorption under the stated conditions; I and II are separated by paper chromatography with butanol - N aq. NH_3 - ethanol (60:27:13) (cf. Gootjes and Nauta, *Anal. Abstr.*, 1955, **2**, 1340). The R_F for I = 0.15, for II = 0.80.

K. SAITO

714. Microbiological and spectrophotometric determination of orotic acid in pharmaceutical preparations. G. Bianchi and E. Lomuto (Res. Dept., Bianchi & Mogli, Firenze, Italy). *Farmaco*, 1959, **14** (3), 175-186.—Details of the microbiological method (*Lactobacillus bulgaricus*) and of a spectrophotometric method are given. The latter is simple, quicker, cheaper and less demanding. *Procedure*—The soln. containing orotic acid or its salts is adjusted to pH 2 and is passed through a chromatographic column (18 cm \times 1.3 cm) packed with activated charcoal previously washed with 0.1 N NaOH, N HCl and H_2O . The column is eluted with acid at pH 2 and the eluates are discarded. The column is then eluted with 0.1 N NaOH (14 \times 5 ml) and the combined eluates are made up to 100 ml with 0.1 N NaOH. The absorption spectrum between 230 $m\mu$ and 330 $m\mu$ is measured against 0.1 N NaOH at 285 $m\mu$. Orotic acid has an extinction ($E_{1\text{cm}}^{1\%}$) of 355.

L. ZANONI

715. Microchemical test for the identification of manna. B. Chiarlo (Ist. Farmacol., Univ. di Genova, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1958, **34** (15), 870-873.—*Procedure*—The sample (4 or 5 mg) is dissolved in a test-tube containing 0.5 ml of reagent [0.5 g of $Bi(NO_3)_3 \cdot 5H_2O$ dissolved in 5 ml of water]. As a control another test-tube containing only the bismuth reagent is used. To the two tubes are added 3 or 4 drops of 1% NaOH soln. The soln. containing manna remains clear while a white ppt. is formed in the control tube. The reaction is given by hexitols other than mannitol, but not by glucose, sucrose, lactose or fructose.

L. ZANONI

716. The micro-fractionation on paper of mixtures of cortisone, deoxycortisone, sodium salicylate and amino acids. H. Chalopin (Fac. de Méd., 12, rue de l'École de Médecine, Paris). *Bull. Soc. Chim. Biol.*, 1959, **41** (2-3), 393-398.—The separation by ascending paper chromatography of mixtures of cortisone and deoxycortisone with Na salicylate and with amino acids, by using water, aq. ethanol soln. and aq. $(NH_4)_2SO_4$ soln. as solvents, has been studied. A good separation of the steroids from Na salicylate is achieved with ethanol containing a little water, and with water containing a little $(NH_4)_2SO_4$. A complete separation of the steroids from amino acids and other substances that give a reaction with ninhydrin is achieved with 40% aq. $(NH_4)_2SO_4$ soln., since the steroids remain near the point of application while the other compounds run with the solvent front. Sulphate soln. do not introduce impurities likely to interfere with the u.v. spectra of the steroids.

D. B. PALMER

717. Chromatographic separation of aldosterone, cortisol and cortisone with a double reversed-phase system. T. Di Perri, G. Ravenni and M. Rubegni (Ist. di Semeiotica Med., Univ. di Siena). *Boll. Soc. Ital. Biol. Sper.*, 1959, **35** (10), 570-573.—Separations of mixed steroids, and of steroids in biological fluids, were carried out at $22^\circ \pm 2^\circ$ on Whatman No. 1 paper saturated with toluene - *n*-octanol (98:2) as the stationary phase, and methanol - water (1:1) as the mobile phase. After being developed for 5 to 6 hr., the papers were dried at room temp. and the steroid spots were located by direct observation in u.v. light, or by u.v. photography. The R_F values were—cortisone, 0.33; aldosterone, 0.47; and cortisol, 0.56. To obtain pure steroids, individual spots were eluted with ethanol, and the eluate was re-chromatographed as described above, but with toluene - light petroleum (1:1) as the stationary phase and methanol - water (7:3) as the mobile phase. In this system, the R_F values were—cortisone, 0.28; aldosterone, 0.43; and cortisol, 0.53. The method is claimed to give better separations than those by conventional procedures in which a stationary aq. phase is used, and the recoveries are almost complete.

C. RAINBOW

718. Determination of barbituric acid derivatives as mercury complexes. C. O. Björling, A. Berggren and B. Willman-Johnson (Res. Lab., Pharmacia Ltd., Uppsala, Sweden). *J. Pharm. Pharmacol.*, 1959, **11** (5), 297-303.—Mix the sample in aq. soln. (<10 ml containing 30 to 300 μ g of barbiturate) with 0.3% mercuric chloride soln. (1 ml) and buffer soln. of pH 8 (1 ml) and extract with $CHCl_3$ (4 \times 10 ml). For phenobarbitone, extract with $CHCl_3$ - dioxan (4:1) (4 \times 10 ml); for barbituric acid, barbitone, allobarbitone, cyclobarbitone or 5-allyl-

702. Determination of morphine in opium. C. A. Teygeler (Rijksinst. v. Pharmacotherapeutisch Onderzoek, Leiden, Netherlands). *Pharm. Weekbl.*, 1959, **94** (7), 201-209.—In an investigation of the Ned. P. VI method, in which the opium extract is purified by passage through alumina followed by the pptn. of morphine by 1-chloro-2:4-dinitrobenzene, errors were found to be due to the adsorption of morphine on the alumina and the co-pptn. of codeine. The pptn. time prescribed (6 hr.) is insufficient, and should be increased to 24 hr.

M. J. MAURICE

703. Assay of reserpine. E. Kahane and M. Kahane (Fac. des Sci., Montpellier, France). *Ann. Pharm. Franç.*, 1958, **16** (12), 726-737.—The micro-Zeisel method for the determination of reserpine is not suitable for dil. soln. The fluorescence and u.v. absorption of soln. have been investigated. The fluorescence of reserpine is accompanied by decomposition and the appearance of a yellow colour, and it is shown that fresh soln. of reserpine do not fluoresce, but that the fluorescence develops under the influence of u.v. light. The u.v. absorption in CHCl_3 gives a max. at $268 \text{ m}\mu$ and a step at $295 \text{ m}\mu$, and the ratio of the extinctions at the max. and the step is 1.83 ± 0.05 . The absorption at $268 \text{ m}\mu$ follows Beer's law. Aged soln. show a change in the ratio. The products of decomposition are removed by passing the soln. through a column of "Hyflo Super-Cel" cellulose, which does not retain the reserpine. Dioxan, methanol and acetic acid can also be used as solvents, methanol being considered the best. Concn. of $20 \mu\text{g}$ per ml are used.

E. J. H. BIRCH

704. Spectrophotometric determination of nicotine. K. Eschle (Reaktor A.-G., Würenlingen, Aargau, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (4), 258-263.—Standard curves for pure nicotine, tobacco "nicotine" and tobacco-smoke "nicotine" are given. They were determined by measuring the maximum of the u.v. extinction with a Beckman spectrophotometer model DU. In contrast to the work of Swain *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 1341) and Willits *et al.* (*Anal. Chem.*, 1950, **22**, 430), considerable differences between the three groups were found. Interfering substances such as pyridine probably account for these discrepancies. For each individual group the standard curve was surprisingly reliable. The results obtained from a large variety of tobaccos, pure and mixed, fermented and unfermented, do not deviate more than 5% from the values of the standard curve.

I. DICKINSON

705. Photometric determination of nicotine in tobacco and tobacco smoke. P. Waltz, M. Häusermann and E. Nyari (Vereinigten Tabakfabriken A.-G., Neuchâtel-Serrières). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (3), 159-165.—The method described is based on that of Wartmann and Harlow (133rd National Meeting of the Amer. Chem. Soc., San Francisco, 1958). Nicotine in tobacco is steam-distilled in the presence of NaCl and NaOH into $N \text{ HCl}$ (15 ml) (soln. A). A 5-ml portion is diluted to 25 ml with 0.05 $N \text{ HCl}$ (soln. B). Extinctions C_1 (at $236 \text{ m}\mu$) and C_2 (at $282 \text{ m}\mu$) are measured on soln. A and C_3 (at $259 \text{ m}\mu$) on soln. B. Then the nicotine (%) in the tobacco is $3856/P[C_2 - (C_1 + C_3)/10]$, where P = wt. (mg) of tobacco taken. The nicotine in smoke is absorbed in CHCl_3 , then extracted with 0.1 $N \text{ H}_2\text{SO}_4$; an aliquot is steam-

distilled after the addition of NaOH and the nicotine determined as described above.

G. BURGER

706. Titration of total alkaloids in *Tabernanthe iboga* roots. G. Ghielmetti and C. Mela (Lab. Ric. Fitochim. "Invernì & Della Beffa" Milano, Italy). *Farmaco*, 1959, **14** (1), 32-36.—*Procedure*—The powdered sample (2 g) is moistened with 2 ml of 10% Na_2CO_3 soln. and mixed with 3 g of Celite. After 2 hr. the mixture is placed in a chromatographic column, and eluted with CHCl_3 , collecting 200 to 250 ml of eluate; this is washed with H_2O in a separating-funnel, dried with anhyd. Na_2SO_4 and evaporated to dryness. The residue is dissolved in acetic acid and titrated with 0.1 $N \text{ HClO}_4$ in acetic acid soln. in the presence of crystal violet as indicator (0.5% in acetic acid soln.), or potentiometrically.

707. Solubility of antibiotics in twenty-four solvents. II. M. L. Andrew and P. J. Weiss (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (5), 277-279.—The solubilities tabulated include those of 16 further salts of the antibiotics studied previously (Weiss *et al.*, *Ibid.*, 1957, **7**, 374) and 22 salts of 14 new antibiotics.

W. H. C. SHAW

708. Dose-response lines for antibiotic microbial assays. A. Kirshbaum, B. Arret and S. D. Harrison (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1959, **9** (5), 301-306.—Statistical procedures are applied to the specific requirements for determining the rectilinear portions of the dose-response curves of microbiological assays. The methods are applied to turbidimetric assays for bacitracin, chloramphenicol, dihydrostreptomycin, oleandomycin, penicillin and tetracycline.

W. H. C. SHAW

709. Control of mixtures of antibiotics by electrophoresis on paper. P. Castel, R. Mus and J. Storck (Fac. de Pharm. de Montpellier, France). *Ann. Pharm. Franç.*, 1959, **17** (1), 63-71.—The following antibiotics (with their mobilities relative to streptomycin) are detected by electrophoresis on paper (Arches No. 301) in a buffer consisting of pyridine 6 ml, acetic acid 20 ml and water to 1 litre, with a p.d. of 225 V—penicillin G (-0.38), Extencillin (benzathine penicillin) (-0.30), oxytetracycline (+0.16), chlortetracycline (+0.16), tetracycline (+0.20), bacitracin (+0.38), carbomycin (+0.40), erythromycin (+0.47), oleandomycin (+0.51), spiramycin (+0.76), quinine penicillin (+0.76), procaine penicillin (+0.76), D-cycloserine (+0.79), viomycin (+0.91), streptomycin (+1.00), framycin (+1.34) and neomycin (+1.36). Reagents for detecting the compounds on the paper are described together with the application of the procedure to known mixtures.

E. J. H. BIRCH

710. Photometric determination of streptomycin and dihydrostreptomycin. E. M. Barilari and M. Katz (Cátedra de Quím. Biol., Univ. Tucumán). *An. Asoc. Quím. Argentina*, 1958, **46** (4), 310-317.—The method is based on measurements of the reducing power with Folin and Wu's reagents.

E. C. APLING

711. Metal chelate compounds of tetracycline derivatives. VIII. Colorimetric determination of tetracycline with boric and sulphuric acids. Keiji Sekiguchi (Pharm. Inst., Med. Fac., Hokkaido Univ., Sapporo). *J. Pharm. Soc. Japan*, 1958, **78**

(9), 965-969.—The colorimetric method of Saka-guchi for the determination of chlortetracycline with H_3BO_3 in conc. H_2SO_4 (cf. *Anal. Abstr.*, 1956, **3**, 520) is applied to the determination of tetracycline (I) (5 to 35 μ g per ml). The max. absorption shifts towards the violet with increase in concn. of H_2SO_4 , the molar extinction coeff. gradually increasing to reach a constant value in H_2SO_4 of concn. $>83.5\%$. Interference results from NO_3^- and NO_2^- . I is separated with an anion-exchange resin (e.g., Dowex 2) by the usual method. The sample soln. (1 ml) is mixed with H_3BO_3 in conc. H_2SO_4 (1% w/v, 9 ml), and the extinction is measured after 1 hr. at 500 $m\mu$. The coeff. of variation is $<\pm 5\%$.

K. SAITO

712. Spectrophotometric assay for chlortetracycline hydrochloride and tetracycline hydrochloride in pharmaceuticals. F. S. Chiccarelli, M. H. Woolford, jun., and M. E. Avery (Lederle Lab. Div., American Cyanamid Co., Pearl River, N.Y.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (5), 263-268.—The method of Chiccarelli *et al.* (cf. *Anal. Abstr.*, 1958, **5**, 1013) has been applied to the determination of chlortetracycline in a number of pharmaceutical preparations. To determine tetracycline in these preparations, prepare an aq. soln. which contains about 200 μ g per ml. To one 5-ml aliquot add 10% $NaHSO_3$ soln. (1 ml) and phosphate buffer (pH 7.5) (10 ml), heat in a bath of boiling water for 3 min., add 5 N HCl (6 ml), heat for 5 min., then cool and dilute with H_2O to 50 ml; heat another 5-ml aliquot (as blank) with $NaHSO_3$ soln. (1 ml) and buffer (pH 7.5) (10 ml) for 3 min., then cool, add 5 N HCl (6 ml) and dilute with H_2O to 50 ml. Measure the extinctions of the two soln. at 434 $m\mu$.

A. R. ROGERS

713. Determination of glycyrrhizic acid in liquorice. Hidehiko Hada and Mizuho Inagaki (Res. Lab., Morishita Jintan Co., 543, Tamahori-cho, Higashi-ku, Osaka). *J. Pharm. Soc. Japan*, 1958, **78** (7), 795-797.—Glycyrrhizic acid (I) gives a max. absorption at 252 $m\mu$ in 40 to 60% (v/v) ethanol and at 258 $m\mu$ in 0.03 to 0.1 N aq. NH_3 , the extinction being proportional to the concn. in the range from 10 to 100 μ g per ml. Glycyrrhetic acid (II), also present in liquorice, gives a similar absorption under the stated conditions; I and II are separated by paper chromatography with butanol-N aq. NH_3 - ethanol (60:27:13) (cf. Gootjes and Nauta, *Anal. Abstr.*, 1955, **2**, 1340). The R_F for I = 0.15, for II = 0.80.

K. SAITO

714. Microbiological and spectrophotometric determination of orotic acid in pharmaceutical preparations. G. Bianchi and E. Lomuto (Res. Dept., Bianchi & Mogli, Firenze, Italy). *Farmaco*, 1959, **14** (3), 175-186.—Details of the microbiological method (*Lactobacillus bulgaricus*) and of a spectrophotometric method are given. The latter is simple, quicker, cheaper and less demanding. *Procedure*—The soln. containing orotic acid or its salts is adjusted to pH 2 and is passed through a chromatographic column (18 cm \times 1.3 cm) packed with activated charcoal previously washed with 0.1 N NaOH, N HCl and H_2O . The column is eluted with acid at pH 2 and the eluates are discarded. The column is then eluted with 0.1 N NaOH (14 \times 5 ml) and the combined eluates are made up to 100 ml with 0.1 N NaOH. The absorption spectrum between 230 $m\mu$ and 330 $m\mu$ is measured against 0.1 N NaOH at 285 $m\mu$. Orotic acid has an extinction ($E_{1\text{cm}}^{1\%}$) of 355.

L. ZANONI

715. Microchemical test for the identification of manna. B. Chiarlo (Ist. Farmacol., Univ. di Genova, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1958, **34** (15), 870-873.—*Procedure*—The sample (4 or 5 mg) is dissolved in a test-tube containing 0.5 ml of reagent [0.5 g of $Bi(NO_3)_3 \cdot 5H_2O$ dissolved in 5 ml of water]. As a control another test-tube containing only the bismuth reagent is used. To the two tubes are added 3 or 4 drops of 1% NaOH soln. The soln. containing manna remains clear while a white ppt. is formed in the control tube. The reaction is given by hexitols other than mannitol, but not by glucose, sucrose, lactose or fructose.

L. ZANONI

716. The micro-fractionation on paper of mixtures of cortisone, deoxycorticosterone, sodium salicylate and amino acids. H. Chalopin (Fac. de Méd., 12, rue de l'École de Médecine, Paris). *Bull. Soc. Chim. Biol.*, 1959, **41** (2-3), 393-398.—The separation by ascending paper chromatography of mixtures of cortisone and deoxycorticosterone with Na salicylate and with amino acids, by using water, aq. ethanol soln. and aq. $(NH_4)_2SO_4$ soln. as solvents, has been studied. A good separation of the steroids from Na salicylate is achieved with ethanol containing a little water, and with water containing a little $(NH_4)_2SO_4$. A complete separation of the steroids from amino acids and other substances that give a reaction with ninhydrin is achieved with 40% aq. $(NH_4)_2SO_4$ soln., since the steroids remain near the point of application while the other compounds run with the solvent front. Sulphate soln. do not introduce impurities likely to interfere with the u.v. spectra of the steroids.

D. B. PALMER

717. Chromatographic separation of aldosterone, cortisol and cortisone with a double reversed-phase system. T. Di Perri, G. Ravenni and M. Rubegni (Ist. di Semeiotica Med., Univ. di Siena). *Boll. Soc. Ital. Biol. Sper.*, 1959, **35** (10), 570-573.—Separations of mixed steroids, and of steroids in biological fluids, were carried out at $22^\circ \pm 2^\circ$ on Whatman No. 1 paper saturated with toluene-n-octanol (98:2) as the stationary phase, and methanol - water (1:1) as the mobile phase. After being developed for 5 to 6 hr., the papers were dried at room temp. and the steroid spots were located by direct observation in u.v. light, or by u.v. photography. The R_F values were—cortisone, 0.33; aldosterone, 0.47; and cortisol, 0.56. To obtain pure steroids, individual spots were eluted with ethanol, and the eluate was re-chromatographed as described above, but with toluene - light petroleum (1:1) as the stationary phase and methanol - water (7:3) as the mobile phase. In this system, the R_F values were—cortisone, 0.28; aldosterone, 0.43; and cortisol, 0.53. The method is claimed to give better separations than those by conventional procedures in which a stationary aq. phase is used, and the recoveries are almost complete.

C. RAINBOW

718. Determination of barbituric acid derivatives as mercury complexes. C. O. Björling, A. Berggren and B. Willman-Johnson (Res. Lab., Pharmacia Ltd., Uppsala, Sweden). *J. Pharm. Pharmacol.*, 1959, **11** (5), 297-303.—Mix the sample in aq. soln. (<10 ml containing 30 to 300 μ g of barbiturate) with 0.3% mercuric chloride soln. (1 ml) and buffer soln. of pH 8 (1 ml) and extract with $CHCl_3$ (4 \times 10 ml). For phenobarbitone, extract with $CHCl_3$ -dioxan (4:1) (4 \times 10 ml); for barbituric acid, barbitone, allobarbitone, cyclobarbitone or 5-allyl-

5-isopropylbarbituric acid, extract with CHCl_3 - benzyl alcohol (4:1) (4×10 ml). Filter the extracts through glass wool, add a 0.0015% soln. of dithizone in CHCl_3 (5 to 40 ml) and dilute with CHCl_3 to 100 ml. Measure the extinction at $605 \text{ m}\mu$ against a reagent blank. The average error is about $\pm 2.5\%$. Low results are obtained in the presence of bromides, iodides and cyanides. Stearic acid, methylthiouracil, propylthiouracil, phenazone and the hydantoin cause positive errors.

A. R. ROGERS

719. Paper-chromatographic identification of barbiturates in toxicological analysis. Swarup Narain Tewari and Dharam Narain Tripathi (Clinical Lab., 18/3A The Mall, Kanpur, India). *Z. anal. Chem.*, 1959, **168** (2), 86-87 (in English).—The material extracted from viscera by repeated boiling with 90% ethanol is dissolved in 0.5% acetic acid, then extracted with diethyl ether and evaporated to dryness. The residue is dissolved in methanol and a drop of the soln. is placed at the centre of a circular sheet of Whatman No. 1 filter-paper. A mixture of isopropyl alcohol, CHCl_3 and 25% aq. NH_3 (5:4:1) is applied by a solvent wick to the centre of the sheet, and the chromatographic chamber is maintained at $10^\circ \pm 1^\circ$. After 30 min. the sheet is removed, dried and examined in u.v. light (254 $\text{m}\mu$). Fluorescent bands indicate the presence of barbiturates. Violet-pink bands are obtained by spraying the sheet with 1% $\text{Co}(\text{NO}_3)_2$ soln. in abs. ethanol, drying and exposing to NH_3 vapour. The bands are compared with those given by known compounds.

S. M. MARSH

720. Identification and determination of some official local anaesthetics as tetraphenylboronates. L. G. Chatten, M. Pernarowski and L. Levi (Food and Drug Directorate, Dept. of Nat. Health and Welfare, Ottawa, Canada). *J. Amer. Pharm. Ass. Sci. Ed.*, 1959, **48** (5), 276-283.—To prepare the tetraphenylboron derivatives of procaine, piperocaine, naepaine, tetracaine, cinchocaine and butethamine, take the hydrochloride of the base (0.2 g) in citrate buffer soln. (pH 6) (20 ml), add 2% Na tetraphenylboron soln. drop by drop with stirring until present in excess, set aside for 1 hr. and collect the ppt. by filtration through sintered glass. Dry *in vacuo* over P_2O_5 for 24 hr. The yield is quant. except with butethamine. These tetraphenylboron derivatives may be analysed by titration in acetone soln. with HClO_4 in glacial acetic acid, with crystal violet as indicator. The u.v. and i.r. absorption spectra of the derivatives are presented.

A. R. ROGERS

721. Micro-determination of Novocain [procaine] and *p*-aminobenzoic acid by a coulometric method after their separation by electrophoresis. K. Kalinowski and Z. Zwierzchowski (Med. Acad., Łódź, Poland). *Acta Polon. Pharm.*, 1958, **15** (3), 175-178.—Procaine (I) and *p*-aminobenzoic acid (II) are separated by electrophoresis. The best results are obtained at pH 5 to 9 (citrate buffer). The zones are detected by Dragendorff's reagent or by diazotisation and coupling with 1-naphthol. The time of separation is 5 to 6 hr. The amounts of I and II may be determined coulometrically in 10% KBr soln. and 15% H_2SO_4 .

H. DMOWSKA

722. Determination of phenylmercury acetate. Kiron Kumar Kundu and Mihir Nath Das (Jadavpur Univ., Calcutta). *Sci. & Cult.*, 1958, **23**, 660-662.—The determination of phenylmercury acetate (I) by

non-aq. titration with 0.1 N HCl in *n*-butanol, with thymol blue (II) or diphenylcarbazide (III) as indicator, is described. In the presence of basic compounds, III but not II can be used as indicator for the titration of I with HCl in alcoholic or glycolic medium. In the presence of Na acetate, III does not show a sharp colour change, and I is determined by titration to a yellow colour with HClO_4 and bromophenol blue in propane-1:3-diol, with CHCl_3 as a solvent; NaCl is added and the liberated Na acetate is titrated. The HClO_4 consumed in the second titration gives the amount of I. In the presence of mercuric acetate, I is dissolved in methanol and one aliquot is titrated with HCl, with II as indicator. To a second aliquot are added a few drops of styrene and the soln. is titrated with HCl after 10 min. If X is the first titre, Y the second, and N is the normality of HCl, then $(2Y - X)N = M$ moles of I.

CHEM. ABSTR.

723. Spectrophotometric determination of *p*-hydroxypropiophenone in several pharmaceutical preparations. M. Mouton and M. Masson (Serv. de Contrôle des Lab. Laroche-Navarron, Leuville-sur-Orge, Seine-et-Oise, France). *Ann. Pharm. Franç.*, 1959, **17** (1), 72-74.—*p*-Hydroxypropiophenone (I) in ethanol has absorption max. at 220 and 275 $\text{m}\mu$. The extinction at 275 $\text{m}\mu$ of soln. and extracts in ethanol (freed from reducing compounds by distilling in the dark from ferricyanide and FeCl_3) of concn. ≈ 1 in 2×10^6 are used for the determination, with pure I as a standard. Phenobarbitone does not interfere but methylthiouracil does, and must be allowed for. A procedure is given for suppositories and ointments.

E. J. H. BIRCH

724. Spectrophotometric determination of cycloheximide. A. A. Forist and S. Theal (Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1042-1044.—The method is based on the reaction with alkaline hydroxylamine to produce a hydroxamic acid, followed by conversion into the highly coloured ferric hydroxamate. The extinction is measured at 530 $\text{m}\mu$, and Beer's law is obeyed over the range 0.2 to 2.2 mg of cycloheximide per ml of sample soln. The mean recovery is 100.2% with a standard deviation of $\pm 1.7\%$ (14 determinations). The results agree well with those obtained by other methods.

G. P. COOK

725. Paper-chromatographic analysis of 8-hydroxyquinoline - Viiform [iodochlorhydroxyquinoline] mixtures. A. Castiglioni (Inst. f. Warenkunde, Turin Univ., Italy). *Z. anal. Chem.*, 1959, **168** (1), 33-34.—Mixtures of 8-hydroxyquinoline (I) and iodochlorhydroxyquinoline (II) may be analysed by chromatographing a soln. with the ascending technique and *n*-butanol - conc. aq. NH_3 (4:1) as the developer. The examination of the dried chromatogram in u.v. light shows the characteristic yellow-green fluorescence of II at the starting point and the yellow fluorescence of I along the liquid front ($R_f \approx 0.9$). Alternatively, the soln. may be subjected to paper electrophoresis in 0.5% aq. NaOH soln. with a current of 2 mA per mm of paper-width for 3 hr. The examination of the dried electropherogram in u.v. light shows both compounds, II having travelled almost twice as far as I. The separation and identification of the two compounds is satisfactory even if only 2 μg of each is present in the mixture.

S. M. MARSH

726. Colorimetric estimation of dithranol [1:8-dihydroxyanthranol]. P. M. Parikh, D. J. Vadodaria and S. P. Mukherji (Zandu Pharm. Works Ltd., Gokhale Road South, Bombay, India). *J. Pharm. Pharmacol.*, 1959, **11** (5), 314-317.—Extract the sample of ointment with hot glacial acetic acid, cool, filter and dilute to give a soln. that contains about 20 µg of dithranol per ml. Mix a 5-ml aliquot with 5% NaNO₃ soln. (1 ml) and heat in a bath of boiling water for 2 min. Cool immediately and dilute with glacial acetic acid to 25 ml. Measure the extinction, with an Ilford 602 filter; use as blank soln. an aliquot treated similarly, but with H₂O (1 ml) in place of NaNO₃ soln. The reproducibility is better than $\pm 2\%$. Zinc oxide, boric acid, benzoic acid and salicylic acid do not interfere.

A. R. ROGERS

727. Detection and determination of meprobamate. **I. Paper partition chromatography.** Masao Shimizu and Shozo Ichimura (Res. Lab., Daiichi Seiyaku Co., Hirakawabashi, Sumida-ku, Tokyo). *J. Pharm. Soc. Japan*, 1958, **78** (10), 1183-1185.—Spots of meprobamate (**I**) are detected with Ehrlich's reagent (2% *p*-dimethylaminobenzaldehyde in conc. HCl) and the *R_F* values are determined with various developing agents. The spot of **I** (*R_F* 0.89) is separated from that of urea (0.46) and NH₄Cl (0.22) with butanol - acetic acid - water (4:1:5). **I** is also separated (*R_F* 0.42) with toluene - butanol (1:1) saturated with formamide, in the presence of amidopyrine (*R_F* 0.85), phenacetin (0.78), sulphapyridine (0) and quinine hydrochloride (0.47).

II. Colorimetric determination with Ehrlich's reagent. Setsuo Sakai, Hajime Mori and Shozo Ichimura. *Ibid.*, 1958, **78** (10), 1185-1187.—In acetic acid, H₂SO₄ or HCl, **I** gives a yellow colour (max. absorption at 416 µm) with Ehrlich's reagent, the extinction coeff. increasing in the order given, and with the concn. of the reagent. Satisfactory results are obtained by making up an ice-cold methanolic soln. of **I**, Ehrlich's reagent (3% in conc. HCl, 10 ml) and methanol to 25 ml and measuring the extinction after 5 min. The calibration curve is linear for < 2 mg of **I** per ml and the colour is stable for 9 hr.

III. Determination of excreted meprobamate in urine. Masao Shimizu, Shozo Ichimura and Hajime Mori. *Ibid.*, 1958, **78** (12), 1374-1377.—By the combination of the methods described above, **I** in urine is satisfactorily determined with an error of < 5%. The sample (≥ 100 ml) is brought to pH 8 with *N* NaOH, filtered and extracted with an equal vol. of diethyl ether and then four times with one half the vol. of ether. The ether is distilled off, and the oily residue is dissolved in methanol and filtered. An aliquot (1 to 2 ml) is submitted to paper chromatography with the toluene - butanol solvent. The zones corresponding to *R_F* 0.3 to 0.65 are cut out, and extracted in a Soxhlet apparatus with methanol (100 ml) for 7 hr., and the extract is evaporated to 5 ml and examined photometrically.

K. SAITO

728. Testing for purity, and the assay of sodium lauryl [dodecyl] sulphate. **II.** P. Schaller (Pharm.-chem. Abt. der Pharm. Inst. der ETH, Zürich). *Pharm. Acta Helv.*, 1959, **34** (5-6), 229-240.—To determine sodium lauryl sulphate in ointments, dissolve the sample in water, or dissolve it in diethyl ether - dioxan (1:1) and extract with water, and apply a modified *p*-toluidine method (cf. Wickbold, *Fette u. Seif.*, 1952, **54**, 394) to the aq. phase. Other alkyl sulphates and aliphatic and aromatic amines interfere.

A. R. ROGERS

729. Determination of low concentrations of some antibacterial substances in solutions after contact with bacteria. A. H. Beckett, S. J. Patki and A. E. Robinson (Sch. of Pharm., Chelsea Coll. of Sci. and Technol., London). *J. Pharm. Pharmacol.*, 1959, **11** (6), 352-359.—Centrifuge the bacterial suspension and extract the supernatant liquid with ether (for chloramphenicol) or with CHCl₃ (for 4-hexylresorcinol, 4-chloro-3:5-xylol or 8-hydroxy-quinoline). Wash the combined organic layers with H₂O, evaporate under reduced pressure, dissolve the residue in H₂O and measure the u.v. absorption. Light-absorbing bacterial exudates are not extracted by the organic solvent and cause no interference.

A. R. ROGERS

See also Abstracts—**585.** Identification of sulphonamides. **642.** Drug concn. in biological fluids. **643.** Isoniazid and 4-aminosalicylic acid in serum. **644.** Pyrazinamide, isoniazid and related compounds in urine. **645.** Meprobamate in urine. **656.** Hesperidin and eriodictin in citrin. **699.** Microbiological assay of antibiotics. **761** to **764.** Determination of folic acid. **765.** Determination of ascorbic acid.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

730. Tin in canned food and foods in general. F. Bucci, A. Cesari and V. Amormino (Ist. Sup. Sanità, Rome). *Chim. e Ind.*, 1959, **41** (4), 294-299.—The sample is ashed with MgO, then fused with KCN and Na₂CO₃, and Sn is determined colorimetrically in an extract of the melt with dithioli. The interference of Cu, which may be present in some products, e.g., tomato purée, can be eliminated by adding KCN to the soln. and filtering. Results for samples of canned and bottled beverages and foods are reported.

C. A. FINCH

731. The "Matveev test" applied to different varieties of hard and soft wheats grown in Algeria. M. Zoubovsky (Centre d'Etude Chim. et Tech. des Blés, Maison Carrée, Algiers). *Ann. Falsif.*, 1959, **52**, 201-206.—The Matveev test for the formation of a ppt. of sterols from soft wheat by cooling an acetone extract of the flour to -5° is modified by the use of a smaller sample; this enables hand-sorting of foreign seeds and very fine grinding to be carried out, and 60 ml of acetone may be used instead of 300 ml. All the varieties (36) of Algerian soft wheat gave a more or less abundant ppt. below -3° . None of the 83 hard wheats gave a ppt. above -4° ; 12 gave a slight flocculent ppt. between -4° and -6° , and 35 gave a ppt. between -6° and -7° . It is recommended that the lower temp. limit for the test should be -5° , and the refrigeration should be carried out in a brine bath to ensure a constant temp.

E. J. H. BIRCH

732. Volumetric determination of the oxidative stability of salted herring. R. Marcuse and K. Knutson (Svenska Inst. för Konserveringsforskning, Göteborg, Sweden). *Grasas y Aceites*, 1959, **10** (2), 97-101.—The stability of salted herring fillets towards oxidation is determined by the volumetric measurement of the uptake of O on storage of the products in closed jars. An evolution of CO₂ accompanies the uptake of O; the CO₂ may be

absorbed in aq. NaOH soln. on a filter-paper cylinder, but in comparative tests (e.g., of different antioxidants) this precaution may be omitted.

L. A. O'NEILL

733. Micro-determination of chloride ions in milk. R. Kh. Zamanov. *Nauch. Trudy Samarkand. Med. Inst.*, 1957, **15**, 311-314; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (18), Abstr. No. 23,592.—*Procedure*—To a milk sample (0.5 to 1 ml) add 0.5 N HNO₃ (0.5 ml), 10% ZnSO₄ (0.3 ml) and ethanol (10 ml), and ethanolic diphenylcarbazone soln. (2 drops) as indicator, and titrate with Hg(NO₃)₂. This method is superior to the Volhard method, which gives lower recoveries.

K. R. C.

734. Separation of strontium-90 from calcium in milk. N. A. Myers (Inst. Cancer Res., Royal Cancer Hospital, London). *Nature*, 1959, **183**, 1807-1808.—Calcium and ⁹⁰Sr in 1 ml of liquid milk can be separated by direct adsorption on to a column (7.5 or 16.5 cm) of Zeo-Karb 225 (50 to 100 mesh, Na form) at 22°, followed by elution with a 1% soln. of EDTA at pH 8 at a flow-rate of 0.2 ml per sq. cm per min. The Ca is in the eluate collected between 6 and 20 ml and the Sr is in that between 20 and 25 ml. Recovery is >90% for both fractions. Retention of casein is zero, nor does the milk fat interfere.

W. J. BAKER

735. Colorimetric determination of added sucrose in milk. R. Biffoli (Lab. Chim. Prov., Firenze, Italy). *Boll. Lab. Chim. Provinciale*, 1959, **10** (2), 116-119.—*Procedure*—Into each of two 100-ml conical flasks is placed 25 ml of milk; to the first is added 2.5 ml of H₂O₂, to the second 2.5 ml of 1% sucrose soln., and 10 ml of 5% uranyl acetate soln. is added to each flask. After 5 min. the soln. are filtered, and an aliquot (10 ml) from each is transferred to 100-ml flasks and 2 ml of satd. ammonium molybdate soln. and 8 ml of N HCl are added. The flasks are heated in a water bath at 80° for 10 min., then cooled, and the soln. are made up to the mark. The blue colour is read in a Lumetron photometer (filter No. 650), deducting 0.065 from the extinction values. The added sucrose (%) is calculated from 0.1 D/D₁ - D, where D is the extinction of the sample and D₁ is the extinction of the sample containing sucrose.

L. ZANONI

736. Isolation of milk phospholipids and determination of their polyunsaturated fatty acids. L. M. Smith and E. L. Jack (California Univ., Davis, U.S.A.). *J. Dairy Sci.*, 1959, **42** (5), 767-779.—The phospholipids (**I**) are separated from other milk lipids by pptn. with acetone, and purified by chromatography on silicic acid - Celite columns. The unsaturated fatty acids are then determined spectroscopically and from iodine values. Alternative procedures for the isolation of **I** are given. A representative sample of **I** from milk contained 26.3% of monoene, 1.5% of conjugated diene and 5.8, 2.4, 1.3 and 1.5% of non-conjugated diene, triene, tetraene and pentaene acids, respectively. The differences between results for these acids in **I** and in milk fat are discussed.

W. H. C. SHAW

737. Relations between composition and viscosity of cows' milk. C. P. Cox, Z. D. Hosking and L. N. Posener (Nat. Inst. Res. Dairying, Shinfield, Reading, England). *J. Dairy Res.*, 1959, **26** (2), 182-189.—Regression analyses have shown that experimental work on the relationship between composition

and viscosity of cows' milk is inadequate, but confirm in general that, with normal milk, the viscosity increases with the fat content at a constant solids-not-fat percentage, and increases with the solids-not-fat content at a constant fat percentage.

W. H. C. SHAW

738. Sugar determination in tomato pulp according to Meissl and Allihi with quantitative sedimentation analysis. IV. W. Kromrey (Sybelstr. 24, Berlin-Charlottenberg, Germany). *Z. Lebensmitteluntersuch.*, 1959, **109** (4), 348-349.—*Procedure for calibration*—Two soln. of glucose monohydrate (5 ml of each, containing respectively 0.5 g and 2.0 g per 100 ml) are mixed with 20 ml of Fehling's soln. No. 1 (**I**) and 10 ml of Fehling's soln. No. 2 (**II**); 7 ml of each mixture is transferred to each of two sedimentation pipettes, which are immersed in boiling water for 5 min., then cooled and centrifuged for 3 min. The supernatant liquid is discarded, the Cu₂O is washed down, and each pipette is centrifuged at 2500 r.p.m. for 3 min. A mean height of 1 mm corresponds to a concn. of glucose of 18.3 mg and 66.5 mg per 100 ml for the two pipettes, with a standard deviation of the height of ± 0.46 and ± 0.48 mm, respectively. *Procedure for tomato pulp*—The sample (5 g) is shaken with 25 ml of water and centrifuged for 15 min.; 20 ml of the supernatant liquid is treated with 10 ml of 10% K₄Fe(CN)₆ soln. and 3 ml of 16% ZnSO₄ soln. plus 7 ml of water, shaken and centrifuged. *Preliminary test*—Aliquots of the supernatant liquid (0.25, 0.5 and 1.5 ml) are mixed with 0.175 ml of **I** and 0.125 ml of **II**, and immersed in boiling water for 10 min. From the colour of the liquid, the pipette to be used, and any required dilution, are selected. *Determination before inversion*—The supernatant liquid (2.5 ml) is mixed with 4 ml of **I** and 2 ml of **II**, heated in boiling water for 5 min. and centrifuged. The Cu₂O is then transferred to the pipette and treated as for the calibration. *Determination after inversion*—The supernatant liquid (2.5 ml) is mixed with conc. HCl (1.5 ml) and heated in boiling water for 10 min. The soln. is then cooled, neutralised with 30% NaOH soln., treated with 4 ml of **I** and 2 ml of **II**, and the procedure continued as before.

S.C.I. ABSTR.

739. Investigation of alginates in dairy products. J. Pien. *Ann. Falsif.*, 1959, **52**, 197-200.—Thickening agents such as alginates, carrageenates (Irish moss), carboxymethylcelluloses, pectin, starch and carob (locust-kernel) gum may be isolated from milk by the method of Fouassim (*Anal. Abstr.*, 1958, **5**, 3521), and identified by the green or green-blue colour given with anthrone and H₂SO₄. Since this reaction is not specific, alginates are detected in the initial residue by means of a reagent consisting of 60 ml of H₂SO₄ (extremely pure) and 10 g of dry Fe₂O₃ (Schroeder and Racicot (*Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 165)), with which alginates give a pink colour changing to red-violet. With 1 mg of alginate the colour may appear in 10 to 20 min., but with less the colour may take a day to develop. With other thickening agents the colour remains a bright yellow.

E. J. H. BIRCH

740. Detection of vegetable thickening agents and polyphosphates, especially in mayonnaise. A. Blumenthal (Chem. Lab. der Stadt, Zürich). *Mitt. Lebensmittel. Hyg., Bern*, 1959, **50** (3), 137-144.—Vegetable thickening agents in concn. down to 0.03% are detected by a modification of Fouassim's

method (*cf. Anal. Abstr.*, 1958, **5**, 3521). The sample of mayonnaise is mixed with milk. Interfering substances are removed by extraction with diethyl ether, pptn. with Luff-Schoorl reagent (aq. soln. of CuSO_4 , citric acid and Na_2CO_3), pptn. with HCl and ethanol and extraction with 50% aq. ethanol. The residual thickening agents give a deep blue to dirty green-brown colour with anthrone (2% in acetic acid) and H_2SO_4 . Individual thickening agents can then be identified by Sulser's paper-chromatographic method (*Mitt. Lebensmittel-Hyg., Bern.*, 1957, **48**, 19). Methylcellulose is detected separately. The mayonnaise is extracted with aq. trichloroacetic acid and filtered. If the filtrate becomes cloudy on boiling and clear on cooling, methylcellulose is indicated, and its presence can be confirmed by pptn. with basic Pb acetate (Sulser's method). Polyphosphates are detected and separately identified in concn. of 0.05% by chromatography of an EDTA (disodium salt) extract. The eluting solvent is an aq. soln. of isopropyl alcohol, conc. aq. NH_3 and trichloroacetic acid. The spots are located with ammonium molybdate and benzidine. G. BURGER

741. Characterisation of colouring matters of vegetable origin by means of paper chromatography. R. Paris and R. Rousset (Lab. de Mat. Méd., Fac. de Pharm., Paris, France). *Ann. Pharm. Franç.*, 1958, **16** (12), 747-756.—Extracts of food and drugs are chromatographed on Whatman No. 1 paper in n -butanol - acetic acid - water (4:1:5) or n -butanol - pyridine - water (1:1:1). The spots are detected by direct visibility or fluorescence, and by 5% KOH soln. for flavone or anthraquinone dyes, 2% FeCl_3 soln. for flavonoids or catechins, 3% HCl for anthocyanins and 10% SbCl_3 in CHCl_3 for carotenoids. Satisfactory spots are given by anthocyanins, alizarin, logwood, brazilin, cutch, chlorophyll, cochineal, turmeric, Persian berry (*Rhamnus infectoria*) extract, indigo carmine, myrtillin, alkanet, archil, purpurin, querцитrin, riboflavin, annatto, saffron, dragon's blood and xanthophyll. Unsatisfactory chromatograms are given by caramel, chicory and indigo. R_f values and colours of the spots are given. E. J. H. BIRCH

742. Polarographic method for determining nitrate in meat and meat-curing brines. J. H. Dhont (Central Inst. for Nutrition and Food Res. T.N.O., Utrecht, Netherlands). *Analyst*, 1959, **84**, 372-375.—Brine (5 to 10 g) is treated with 1 ml of 6% urea soln. and 0.1 ml of 19% HCl; the mixture is set aside for 1 hr., then diluted to 250 ml. A 25-ml aliquot is treated with 5 ml of 20% Pb acetate soln., diluted to 50 ml and filtered. Two equal aliquots (5 to 10 ml), to one of which 0.5 ml of standard KNO_3 soln. (0.2%) has been added, are evaporated to dryness and heated for a few minutes in an oven at 110° to 120°. To each cooled residue a specified phenoldisulphonic acid reagent is added and the mixture is heated on the water bath for ≥ 3 min. and then adjusted with water to 10 ml. The soln., including any ppt., is placed in the electrolysis cell of a polarograph, O is removed by means of a stream of N, and the diffusion current at 0.00 to -0.60 V is measured against the mercury-pool anode and corrected for the blank value. The concn. of NO_3^- in the sample is calculated from the increase of diffusion current caused by the addition of standard KNO_3 soln. The procedure for meat and meat products is similar, with the inclusion of a disintegration procedure in a Waring Blender after the

treatment with urea and HCl. The recovery of known amounts of added KNO_3 was good.

A. O. JONES

743. Modified direct colorimetric method for determination of sulphur dioxide in dried fruits. F. S. Nury, D. H. Taylor and J. E. Brekke (W. Regional Res. Lab., Agric. Res. Service, U.S. Dept. of Agric., Albany, Calif., U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (6), 351-353.—The method of West and Gaeke (*cf. Anal. Abstr.*, 1957, **4**, 1817) as modified by Stone and Laschiver (*Wallerstein Labs Commun.*, 1957, **20**, 361) provides a method suitable for both field and laboratory work; the results agree well with those obtained by the gravimetric Monier-Williams method. *Procedure*—Macerate 10 g of dried fruit with 290 ml of water for 3 to 5 min. Mix a 10-ml aliquot for 15 to 30 sec. with 4 ml of 0.5 N NaOH in a 100-ml flask, add 4 ml of 0.5 N H_2SO_4 , followed by 20 ml of sodium tetrachloromercurate soln. (23.4 g of NaCl and 54.3 g of HgCl_2 in 2 litres of water), and dilute to the mark. With dried apples, 2 ml, and with golden bleached raisins, 1 ml, of the acid and alkali are required. To 2-ml aliquots of the filtered or decanted soln. mixed with 5 ml of acid-bleached pararosaniline hydrochloride soln. (80 ml of HCl added to 100 mg of the dye in 280 ml of water and diluted to 1 litre with water on the previous day) add 10 ml of 0.016% formaldehyde soln.; mix, and after 20 to 30 min. at room temp. measure the extinction of the soln. at 550 to 570 μm . Carry out a blank determination on the fruit, with 10 ml of water in place of the aldehyde soln. Determine the amount of SO_2 by reference to a standard curve prepared by plotting the extinctions of colours developed similarly by 2-ml aliquots of standard aq. soln. containing 0 to 50 μg of $\text{Na}_2\text{S}_2\text{O}_5$ and 0.2 ml of the sodium tetrachloromercurate soln. per ml against SO_2 concn. The free SO_2 content of dried fruit may be determined by omitting the addition of the acid and alkali. S. C. JOLLY

744. General method for the detection of preservatives in beverages. A. Canuti (Lab. Chim. Prov., Frosinone, Italy). *Boll. Lab. Chim. Provinciati*, 1959, **10** (2), 145-151.—*Procedure*—To 50 ml of sample, diluted to 100 ml with H_2O and adjusted to pH 8.4 with 5% Na_2CO_3 soln., is added 2 ml of a 2% suspension of *Saccharomyces cerevisiae* at pH 8.4. The mixture is incubated at 37° and the change in pH is followed. A stationary pH indicates the presence of preservatives. A blank must be carried out. The method is very sensitive and can be applied to other foods. L. ZANONI

745. Determination of orange juice in beverages. R. Intonti, F. C. Ramusino and A. Stacchini (Ist. Sup. Sanità, Roma, Italy). *Ind. Conserve, Parma*, 1959, **34** (3), 222-227.—The method is based on the determination of formaldehyde number. *Procedure*—The sample (200 ml of beverage or 20 g of juice diluted to 200 ml) is concentrated in a porcelain dish on a water bath at 80° for 2 hr. The cooled soln. is neutralised to pH 8 (potentiometer), by first adding N NaOH and then 0.1 N NaOH. Formaldehyde soln. (40%) (20 ml), previously neutralised to pH 8, is added; in the presence of orange juice the pH will decrease. The soln. is then titrated with 0.1 N NaOH to pH 8. The titre (ml) divided by 2 represents the formaldehyde number (F), and the amount (in g) of orange juice contained in 100 ml of sample is given by $1.05 F/1.4$. L. ZANONI

746. Calculation of original wort in beer. M. Brofeldt. *Brauissenschaft*, 1959, **12** (5), 121-128.—The author's formula (*Ibid.*, 1957, **10**, 202, 313) and a modified Balling formula for the calculation of original wort in beer, and the Tabarié and Reischauer formulae for calculating apparent-extract content are discussed. Formulae of the type $p = 100 (C \times A + m)/(100 + A)$ with $C = 2.50$ and $p = 100 (k \times A + n)/(100 + A)$ with $k = 2.03$, where p = original wort, and A , m and n = the % by wt. of alcohol, apparent extract and real extract, respectively, of the beer, have yielded good results with Danish and Finnish beers, and with suitable coeff. can be used for bottom- and top-fermentation German beers. **S.C.I. ABSTR.**

747. Determination of iron in beer. W. Kleber, P. Schmid and G. Franke (Wissenschaftl. Sta. f. Brauerei, München, Germany). *Brauissenschaft*, 1959, **12** (5), 119-121.—Results obtained by the 2:2'-dipyridyl method without decomposition of the organic matter were lower than when the organic matter was decomposed, but the lower results increased if the reaction time was lengthened (e.g., to 18 hr.). This is explained on mass-action principles. As the properties of beer are influenced by Fe both in the ionised state and when bound in complexes, the total Fe content must be determined. The method differentiates between ionised and bound Fe. **S.C.I. ABSTR.**

748. Complexometric titration of calcium in wine. R. Bifoli (Lab. Chim. Prov., Firenze, Italy). *Boll. Lab. Chim. Provinciale*, 1959, **10** (2), 120-123.—The Ca is ptdt. as oxalate, which is dissolved in 0.5 N HCl. Murexide indicator is then added, followed by adjustment of the pH to 12 with 2 N KOH, and the Ca is titrated with 0.01 M EDTA. **L. ZANONI**

749. Determination of fluorine in wine. F. Bucci and P. Tandoi (Ist. Sup. Sanita, Rome). *Chim. e Ind.*, 1959, **41** (4), 299-303.—Existing methods are reviewed. A new method is described, based on the ashing of the sample with MgO, and the isolation of F as fluorosilicic acid by steam-distillation in the presence of H_2SO_4 . Fluorine in the distillate is determined colorimetrically, by the fading of a Zr-alizarinsulphonic acid lake through the complexing of the F-. The apparatus is described. Some possible interferences are discussed. **C. A. FINCH**

750. Potentiometric semi-micro determination of saponification value. P. A. Gutiérrez Amo and D. Martín (Inst. L. Torres Quevedo, Madrid). *Grasas y Aceites*, 1959, **10** (1), 12-13.—The sample, e.g., olive or soya-bean oil (0.4 to 0.5 g) is saponified with 5 ml of 3% ethanolic KOH for 30 min. on a water bath and then titrated potentiometrically with 0.5 N HCl in 96% ethanol, the double endpoint method being used. The effect of the H_2O content of the ethanol and possible causes of errors have been examined. **L. A. O'NEILL**

751. The acidity of olive oils and its determination. A. Teissier. *Ann. Falsif.*, 1959, **52**, 207-214.—In order to explain the differences in determinations of the acidity of crude olive oils (particularly of Moroccan origin, 1956-57) a sample of oil was treated in different ways. The acidity was determined after a short period of settling and decantation, after a long period of settling, after filtering and after washing with warm water. The acidity of the

decanted oil is higher than that of the filtered oil, but it is shown that the aqueous deposit obtained by a short settling period is not sufficiently acid to affect the result, and the discrepancy is attributed to water-soluble acidity slowly released from the oil, since seven washings with warm water are required before the washings are neutral. It is concluded that the prescribed method of filtering the oil on paper, after heating, is necessary and that the filter-paper does not retain any fatty acids from the oil. **E. J. H. BIRCH**

752. Ultra-violet spectrophotometric studies of olive oil. B. Doro and V. Sadini (Lab. Chim. Prov., Trieste, Italy). *Boll. Lab. Chim. Provinciale*, 1959, **10** (2), 124-144.—From a study of the u.v. absorption spectra, the values of K_{232} , K_{270} and R ($= K_{232}/K_{270}$) are established for virgin oils, and "rectified A" and "rectified B" oils. These are as follows—virgin oil, K_{232} between 1.61 and 2.83; K_{270} between 0.12 and 0.24; and R between 10 and 15. In rancid oils R can fall to 7; rectified A oil, K_{232} between 2.0 and 2.7; K_{270} between 0.5 and 1.0; and R between 2.8 and 4.2; rectified B oil, K_{232} between 4.5 and 8.4; K_{270} between 1.3 and 3.4; and R between 1.8 and 4.2. From these figures it is possible to distinguish virgin olive oil, and to detect the addition thereto of <10% of rectified oils. **L. ZANONI**

753. Determination of impurities and "oxidised acids" in sulphur olive oil and its industrial evaluation. J. Gracián and M. Ventura (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1959, **10** (2), 67-75.—The effect of different solvents for determining the content of impurities in sulphur olive oil, the effect of removing the impurities from the oil before the determination of the "oxidised acids" (acids insol. in light petroleum), and the changes in the amounts of impurities and oxidised acids in oils on storage have been studied. It is suggested that an oil might be assessed on the basis of its total fatty acid content instead of on the amount of H_2O , impurities and oxidised acids present. **L. A. O'NEILL**

754. Measurement of radial paper chromatograms of unsaturated fatty acids with a microphotometer. H. Sulser (Lab. des Eidg. Gesundheitsamtes, Bern, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (4), 275-286.—The difficulties of identifying fatty acids with similar analytical values, and of distinguishing them from synthetic fats, led to the development of accurate measurements of paper chromatograms. *Procedure*—A mixture of fatty acids (450 mg) was dissolved in 2 ml of $CHCl_3$; 5 μ l was transferred to a paper strip impregnated with liquid paraffin and developed radially with 84% acetic acid soln. for ≈ 20 hr. The colouring of the fatty acids was carried out with periodate-permanganate-benzidine (*cf. Anal. Abstr.*, 1959, **6**, 1534). The chromatograms were then photographed, diapositives were made and measured with a microphotometer. From the values, bell-shaped curves were obtained, the areas of which can be measured with a planimeter, or the areas can be cut out and weighed. An accuracy within $\pm 10\%$ can be expected. Results are given for synthetic mixtures of pure oleic and linoleic acids. **I. DICKINSON**

755. Mass spectra of methyl oleate, methyl linoleate and methyl linolenate. B. Hallgren, R. Ryhage and E. Stenhagen (Inst. Med. Biochem.,

Gothenburg, Sweden). *Acta Chem. Scand.*, 1959, **13** (4), 845-847.—The spectra were obtained with the apparatus and procedure described by Ryhage (*Ark. Kemi*, 1959, **13**, 475). The fragmentation patterns obtained differed from those of the methyl esters of saturated long-chain fatty acids in that the low mass peaks due to fragments containing an intact methoxycarbonyl group were much less prominent and the peaks due to hydrocarbon fragments correspondingly more so. It is concluded that it is not possible to determine the position of the double-bond in an unsaturated fatty acid by direct mass spectrometry.

W. T. CARTER

756. Determination of the vitamins in vegetable and fruit products by infra-red spectrometry. E. Bottini and A. Zavanayu (Staz. Chim. Agrar. Sper., Torino, Italy). *Ann. Sper. Agr.*, 1957, **12** (5), 1233-1283.—The determination of vitamins in preparations of vegetable origin is discussed. The disadvantages of many of the present chemical and biological methods are indicated, and a new method of identification by means of i.r. spectrometry is given. *Procedure*—A soln. in a non-aq. solvent is allowed to evaporate on a sodium chloride plate, which is interposed in a beam of infra-red rays. The measurement is carried out with a Perkin-Elmer infra-red spectrophotometer. The absorption curves of vitamin A, members of the B group and ascorbic acid are given. These have a number of specific bands which permit the identification of the vitamins.

L. ZANONI

757. Rapid control of the vitamin-A content of vitaminised feeding-stuffs. P. Mazzotti di Celso (Ist. Sper. Zootecnico, Roma, Italy). *Ann. Sper. Agr.*, 1958, **12** (2), Suppl. I-111.—The procedure is based on the ready extractability of added vitamin A. *Procedure*—The feeding-stuff (2 to 5 g) is extracted with successive portions of light petroleum (b.p. 40°), the extract is transferred to a separating-funnel, and saponified by continual shaking at room temp. with an equal vol. of ethanolic KOH (5% of KOH in 90% ethanol). The ethanolic phase is discarded. The light-petroleum phase is washed twice with H_2O , once with 1% H_2SO_4 and four times with H_2O , and is then treated with anhyd. Na_2SO_4 and filtered, and the solvent is removed by heating at 40° in a stream of N. The residue is dissolved in cyclohexane (5 ml) and 1 ml of this soln. is made up to 5 ml. The extinction is measured with a Beckman DU spectrophotometer using the Morton correction.

L. ZANONI

758. Chemical determination of vitamin D. H. Tschapke (Inst. Nutr., Potsdam-Rehbrücke, Germany). *Nahrung*, 1958, **2**, 44-49.—The vitamin D is extracted with ether, and vitamin A and similar compounds are removed by adsorption on activated talc. The ether soln. is evaporated, the residue is dissolved in $CHCl_3$, and a 2-ml aliquot is treated with 1 ml of a freshly prepared $SnCl_2$ soln. [0.1 g of $SnCl_2 \cdot 2H_2O$ is shaken with 10 ml of freshly distilled acetyl chloride and filtered through a double filter-paper layer; the filtrate is used]. The extinction of the resulting soln. is measured at $\approx 500 m\mu$, after 3 min. for vitamin D_3 and after 90 sec. for vitamin D_2 . Analyses by this method give results in good agreement with those of biological assays, and are easier to perform.

CHEM. ABSTR.

759. Physico-chemical method for estimation of thiamine, pyridoxine and nicotinamide in the presence of riboflavin and panthenol. D. K.

Bardhan, R. N. Bhattacharya and S. K. Dutta (Bengal Immunity Res. Inst., Calcutta). *Sci. & Cult.*, 1958, **24** (2), 85-86.—The u.v. spectra of the vitamins of the B group were studied at various pH values in aq. and in buffer soln. With the exception of panthenol and pantothenic acid, all have high absorptions in the u.v. region; riboflavin fluoresces so strongly that the direct spectrophotometric determination of the other vitamins present is almost impossible, unless the riboflavin is removed by the use of ion-exchange resin. The preparation (5 ml) is passed through a column of Decolorite anion-exchange resin at ≈ 1 drop per sec.; riboflavin is completely adsorbed and the extinctions at 247 $m\mu$, 260 $m\mu$ and 290 $m\mu$ are determined on the percolate. The concn. of thiamine, pyridoxine and nicotinamide are calculated with an accuracy of $\pm 6\%$ from equations involving the known extinctions of these compounds at the given wavelengths.

K. R. C.

760. Determination of "OS-dibenzoylthiamine" and "thiamine 2-hydroxyethyl disulphide." Makoto Hoshino and Masamichi Kuriyama. *Ann. Rep. Takeda Res. Lab.*, 1958, **17**, 105-110.—Samples were prepared by mixing pure OS-dibenzoylthiamine (**I**) or thiamine 2-hydroxyethyl disulphide (**II**) with their usual impurities in various ratios. Each sample was subjected to paper electrophoresis in 30% acetic acid for 3 hr. at 300 V per 40 cm and the migrated spots, detected under u.v. light, were cut out and extracted with 0.01 N HCl for **I** and with 0.1 N HCl for **II**. Extinctions at 237 and 265 $m\mu$ for **I** or at 243 $m\mu$ for **II** in the extracts were measured to determine their components. With **I**, O-benzoylthiamine and thiamine, which were added as impurities, were determined simultaneously, and, with **II**, thiamine disulphide and thiamine were also determined simultaneously. **I** can be determined in the presence of $Ba(OH)_2$, and **II** in the presence of thiochrome, thiothiamine, 2-mercaptoethanol and thiamine-thiazolone.

CHEM. ABSTR.

761. Folic acid. New colorimetric determination. G. Vergés. *Farm. Nueva, Madrid*, 1958, **23**, 419-422.—The method is based on the colour developed when a soln. of folic acid (**I**) in HNO_3 is boiled and then treated with aq. NH_3 . The Beer-Lambert law is obeyed and the extinction of the soln. is measured photometrically with a 485- $m\mu$ blue filter. **I** (20 mg) of known purity is dissolved in 10 ml of HNO_3 ; 1 ml of this soln. is further diluted with HNO_3 (9 ml), and used for preparing a standard curve. This method can be used to analyse samples containing as little as 8.33 μg of **I** per ml. A brief discussion of existing biological, microbiological, gravimetric, fluorimetric, polarographic and absorption methods of determining **I** is included.

CHEM. ABSTR.

762. Micro-determination of folic acid by coulometric and titrimetric methods using chloramine T. K. Kalinowski and Z. Sykulski (Med. Acad., Łódź, Poland). *Acta Polon. Pharm.*, 1958, **15** (3), 179-184.—A coulometric method depending on the reaction of electrolytically produced Cl with folic acid (1 mol. of folic acid $\equiv 4Cl_2$) and a method depending on direct titration with chloramine T are described.

H. DMOWSKA

763. Ultra-micro method for assay of pteroylglutamic acid (folic acid) activity. W. N. Pearson, E. R. Brodovsky, E. R. Carnes and W. J. Darby

746. Calculation of original wort in beer. M. Brofeldt. *Brauwissenschaft*, 1959, **12** (5), 121-128.—The author's formula (*Ibid.*, 1957, **10**, 202, 313) and a modified Balling formula for the calculation of original wort in beer, and the Tabarié and Reischauer formulae for calculating apparent-extract content are discussed. Formulae of the type $p = 100 (C + A + m)/(100 + A)$ with $C = 2.50$ and $p = 100 (k \times A + n)/(100 + A)$ with $k = 2.03$, where p = original wort, and A , m and n = the % by wt. of alcohol, apparent extract and real extract, respectively, of the beer, have yielded good results with Danish and Finnish beers, and with suitable coeff. can be used for bottom- and top-fermentation German beers. S.C.I. ABSTR.

747. Determination of iron in beer. W. Kleber, P. Schmid and G. Franke (Wissenschaftl. Sta. f. Brauerei, München, Germany). *Brauwissenschaft*, 1959, **12** (5), 119-121.—Results obtained by the 2:2'-dipyridyl method without decomposition of the organic matter were lower than when the organic matter was decomposed, but the lower results increased if the reaction time was lengthened (e.g., to 18 hr.). This is explained on mass-action principles. As the properties of beer are influenced by Fe both in the ionised state and when bound in complexes, the total Fe content must be determined. The method differentiates between ionised and bound Fe. S.C.I. ABSTR.

748. Complexometric titration of calcium in wine. R. Biffoli (Lab. Chim. Prov., Firenze, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (2), 120-123.—The Ca is ptdt. as oxalate, which is dissolved in 0.5 N HCl. Murexide indicator is then added, followed by adjustment of the pH to 12 with 2 N KOH, and the Ca is titrated with 0.01 M EDTA. L. ZANONI

749. Determination of fluorine in wine. F. Bucci and P. Tandoi (Ist. Sup. Sanità, Rome). *Chim. e Ind.*, 1959, **41** (4), 299-303.—Existing methods are reviewed. A new method is described, based on the ashing of the sample with MgO, and the isolation of F as fluorosilicic acid by steam-distillation in the presence of H_2SO_4 . Fluorine in the distillate is determined colorimetrically, by the fading of a Zr-alizarinsulphonic acid lake through the complexing of the F^- . The apparatus is described. Some possible interferences are discussed. C. A. FINCH

750. Potentiometric semi-micro determination of saponification value. P. A. Gutiérrez Amo and D. Martín (Inst. L. Torres Quevedo, Madrid). *Grasas y Aceites*, 1959, **10** (1), 12-13.—The sample, e.g., olive or soya-bean oil (0.4 to 0.5 g) is saponified with 5 ml of 3% ethanolic KOH for 30 min. on a water bath and then titrated potentiometrically with 0.5 N HCl in 96% ethanol, the double endpoint method being used. The effect of the H_2O content of the ethanol and possible causes of errors have been examined. L. A. O'NEILL

751. The acidity of olive oils and its determination. A. Teissier. *Ann. Faitsf.*, 1959, **52**, 207-214.—In order to explain the differences in determinations of the acidity of crude olive oils (particularly of Moroccan origin, 1956-57) a sample of oil was treated in different ways. The acidity was determined after a short period of settling and decantation, after a long period of settling, after filtering and after washing with warm water. The acidity of the

decanted oil is higher than that of the filtered oil, but it is shown that the aqueous deposit obtained by a short settling period is not sufficiently acid to affect the result, and the discrepancy is attributed to water-soluble acidity slowly released from the oil, since seven washings with warm water are required before the washings are neutral. It is concluded that the prescribed method of filtering the oil on paper, after heating, is necessary and that the filter-paper does not retain any fatty acids from the oil. E. J. H. BIRCH

752. Ultra-violet spectrophotometric studies of olive oil. B. Doro and V. Sadini (Lab. Chim. Prov., Trieste, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (2), 124-144.—From a study of the u.v. absorption spectra, the values of K_{282} , K_{370} and R (= K_{282}/K_{370}) are established for virgin oils, and "rectified A" and "rectified B" oils. These are as follows—virgin oil, K_{282} between 1.01 and 2.83; K_{370} between 0.12 and 0.24; and R between 10 and 15. In rancid oils R can fall to 7; rectified A oil, K_{282} between 2.0 and 2.7; K_{370} between 0.5 and 1.0; and R between 2.8 and 4.2; rectified B oil, K_{282} between 4.5 and 8.4; K_{370} between 1.3 and 3.4; and R between 1.8 and 4.2. From these figures it is possible to distinguish virgin olive oil, and to detect the addition thereto of <10% of rectified oils. L. ZANONI

753. Determination of impurities and "oxidised acids" in sulphur olive oil and its industrial evaluation. J. Gracián and M. Ventura (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1959, **10** (2), 67-75.—The effect of different solvents for determining the content of impurities in sulphur olive oil, the effect of removing the impurities from the oil before the determination of the "oxidised acids" (acids insol. in light petroleum), and the changes in the amounts of impurities and oxidised acids in oils on storage have been studied. It is suggested that an oil might be assessed on the basis of its total fatty acid content instead of on the amount of H_2O , impurities and oxidised acids present. L. A. O'NEILL

754. Measurement of radial paper chromatograms of unsaturated fatty acids with a microphotometer. H. Sulser (Lab. des Eidg. Gesundheitsamtes, Bern, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (4), 275-286.—The difficulties of identifying fatty acids with similar analytical values, and of distinguishing them from synthetic fats, led to the development of accurate measurements of paper chromatograms. *Procedure*—A mixture of fatty acids (400 mg) was dissolved in 2 ml of $CHCl_3$; 5 μ l was transferred to a paper strip impregnated with liquid paraffin and developed radially with 84% acetic acid soln. for ≥ 20 hr. The colouring of the fatty acids was carried out with periodate-permanganate-benzidine (*cf. Anal. Abstr.*, 1959, **6**, 1534). The chromatograms were then photographed, diapositives were made and measured with a microphotometer. From the values, bell-shaped curves were obtained, the areas of which can be measured with a planimeter, or the areas can be cut out and weighed. An accuracy within $\pm 10\%$ can be expected. Results are given for synthetic mixtures of pure oleic and linoleic acids. I. DICKINSON

755. Mass spectra of methyl oleate, methyl linoleate and methyl linolenate. B. Hallgren, R. Ryhage and E. Stenhammar (Inst. Med. Biochem.,

Gothenburg, Sweden). *Acta Chem. Scand.*, 1959, **13** (4), 845-847.—The spectra were obtained with the apparatus and procedure described by Ryhage (*Ark. Kemi*, 1959, **13**, 475). The fragmentation patterns obtained differed from those of the methyl esters of saturated long-chain fatty acids in that the low mass peaks due to fragments containing an intact methoxycarbonyl group were much less prominent and the peaks due to hydrocarbon fragments correspondingly more so. It is concluded that it is not possible to determine the position of the double-bond in an unsaturated fatty acid by direct mass spectrometry.

W. T. CARTER

756. Determination of the vitamins in vegetable and fruit products by infra-red spectrometry. E. Bottini and A. Zavanay (Staz. Chim. Agrar. Sper., Torino, Italy). *Ann. Sper. Agr.*, 1957, **12** (5), 1233-1283.—The determination of vitamins in preparations of vegetable origin is discussed. The disadvantages of many of the present chemical and biological methods are indicated, and a new method of identification by means of i.r. spectrometry is given. *Procedure*—A soln. in a non-aq. solvent is allowed to evaporate on a sodium chloride plate, which is interposed in a beam of infra-red rays. The measurement is carried out with a Perkin-Elmer infra-red spectrophotometer. The absorption curves of vitamin A, members of the B group and ascorbic acid are given. These have a number of specific bands which permit the identification of the vitamins.

L. ZANONI

757. Rapid control of the vitamin-A content of vitaminised feeding-stuffs. P. Mazzotti di Celso (Ist. Sper. Zootecnico, Roma, Italy). *Ann. Sper. Agr.*, 1958, **12** (2), Suppl. I-111.—The procedure is based on the ready extractability of added vitamin A. *Procedure*—The feeding-stuff (2 to 5 g) is extracted with successive portions of light petroleum (b.p. 40°), the extract is transferred to a separating-funnel, and saponified by continual shaking at room temp. with an equal vol. of ethanolic KOH (5% of KOH in 90% ethanol). The ethanolic phase is discarded. The light-petroleum phase is washed twice with H_2O , once with 1% H_2SO_4 and four times with H_2O , and is then treated with anhyd. Na_2SO_4 and filtered, and the solvent is removed by heating at 40° in a stream of N. The residue is dissolved in cyclohexane (5 ml) and 1 ml of this soln. is made up to 5 ml. The extinction is measured with a Beckman DU spectrophotometer using the Morton correction.

L. ZANONI

758. Chemical determination of vitamin D. H. Tschapke (Inst. Nutr., Potsdam-Rehbrücke, Germany). *Nahrung*, 1958, **2**, 44-49.—The vitamin D is extracted with ether, and vitamin A and similar compounds are removed by adsorption on activated talc. The ether soln. is evaporated, the residue is dissolved in $CHCl_3$, and a 2-ml aliquot is treated with 1 ml of a freshly prepared $SnCl_4$ soln. [0.1 g of $SnCl_4 \cdot 2H_2O$ is shaken with 10 ml of freshly distilled acetyl chloride and filtered through a double filter-paper layer; the filtrate is used]. The extinction of the resulting soln. is measured at $\approx 500 m\mu$, after 3 min. for vitamin D_3 and after 90 sec. for vitamin D_2 . Analyses by this method give results in good agreement with those of biological assays, and are easier to perform.

CHEM. ABSTR.

759. Physico-chemical method for estimation of thiamine, pyridoxine and nicotinamide in the presence of riboflavin and panthenol. D. K.

Bardhan, R. N. Bhattacharya and S. K. Dutta (Bengal Immunity Res. Inst., Calcutta). *Sci. & Cult.*, 1958, **24** (2), 85-86.—The u.v. spectra of the vitamins of the B group were studied at various pH values in aq. and in buffer soln. With the exception of panthenol and pantothenic acid, all have high absorptions in the u.v. region; riboflavin fluoresces so strongly that the direct spectrophotometric determination of the other vitamins present is almost impossible, unless the riboflavin is removed by the use of ion-exchange resin. The preparation (5 ml) is passed through a column of Decolorite anion-exchange resin at ≈ 1 drop per sec.; riboflavin is completely adsorbed and the extinctions at 247 $m\mu$, 260 $m\mu$ and 290 $m\mu$ are determined on the percolate. The concn. of thiamine, pyridoxine and nicotinamide are calculated with an accuracy of $\pm 6\%$ from equations involving the known extinctions of these compounds at the given wavelengths.

K. R. C.

760. Determination of "OS-dibenzoylthiamine" and "thiamine 2-hydroxyethyl disulphide." Makoto Hoshino and Masamichi Kuriyama. *Ann. Rep. Takeda Res. Lab.*, 1958, **17**, 105-110.—Samples were prepared by mixing pure OS-dibenzoylthiamine (**I**) or thiamine 2-hydroxyethyl disulphide (**II**) with their usual impurities in various ratios. Each sample was subjected to paper electrophoresis in 30% acetic acid for 3 hr. at 300 V per 40 cm and the migrated spots, detected under u.v. light, were cut out and extracted with 0.01 N HCl for **I** and with 0.1 N HCl for **II**. Extinctions at 237 and 265 $m\mu$ for **I** or at 243 $m\mu$ for **II** in the extracts were measured to determine their components. With **I**, O-benzoylthiamine and thiamine, which were added as impurities, were determined simultaneously, and, with **II**, thiamine disulphide and thiamine were also determined simultaneously. **I** can be determined in the presence of $Ba(OH)_2$, and **II** in the presence of thiocchrome, thiothiamine, 2-mercaptoethanol and thiamine-thiazolone.

CHEM. ABSTR.

761. Folic acid. New colorimetric determination. G. Vergés. *Farm. Nueva, Madrid*, 1958, **23**, 419-422.—The method is based on the colour developed when a soln. of folic acid (**I**) in HNO_3 is boiled and then treated with aq. NH_3 . The Beer-Lambert law is obeyed and the extinction of the soln. is measured photometrically with a 485- $m\mu$ blue filter. **I** (20 mg) of known purity is dissolved in 10 ml of HNO_3 ; 1 ml of this soln. is further diluted with HNO_3 (9 ml), and used for preparing a standard curve. This method can be used to analyse samples containing as little as 8.33 μg of **I** per ml. A brief discussion of existing biological, microbiological, gravimetric, fluorimetric, polarographic and absorptiometric methods of determining **I** is included.

CHEM. ABSTR.

762. Micro-determination of folic acid by coulometric and titrimetric methods using chloramine T. K. Kalinowski and Z. Sykulski (Med. Acad., Łódź, Poland). *Acta Polon. Pharm.*, 1958, **15** (3), 179-184.—A coulometric method depending on the reaction of electrolytically produced Cl with folic acid (1 mol. of folic acid = $4Cl_4$) and a method depending on direct titration with chloramine T are described.

H. DMOWSKA

763. Ultra-micro method for assay of pteroylglutamic acid (folic acid) activity. W. N. Pearson, E. R. Brodovsky, E. R. Carnes and W. J. Darby

(Vanderbilt Univ. Sch. Med., Nashville, Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (6), 1113-1114.—The usual macro-method for the assay of folic acid with *Streptococcus faecalis* as the test organism was modified for sub-micro levels. Folic acid concn. of 0.01 to 0.1 μ g in a sample volume of 0.2 ml were determined titrimetrically. The results agreed well with those obtained by the macro-method.

G. P. COOK

764. Chromatography of pteroylglutamic acid (folic acid) and related compounds on ion-exchange resins. M. R. Heinrich, V. C. Dewey and G. W. Kidder (Biol. Lab., Amherst Coll., Mass., U.S.A.). *J. Chromatography*, 1959, **2** (3), 296-303.—Anion-exchange chromatography on Dowex-1 resin (chloride form) (4% cross-linked) has been applied to the separation and purification of free and conjugated pteridines. The compounds are applied to the column in a small vol. of water brought to pH 8 to 9 with aq. NH_3 . Elution is carried out with very dilute HCl or NaCl soln. and the column and fraction collector are excluded from light. The following compounds have been successfully adsorbed and eluted—biopterin, leucopterin, xanthopterin, pteroylglutamic acid (PGA), leucovorin, 10-formyl-PGA, aminopterin, methotrexate and Methopterin (10-methyl-PGA). Elution with formic acid from Dowex-1 resin (formate form) produces separation of the monoamino- and diamino-folic acid compounds, but no resolution within each group. During chromatography an appreciable degree of formylation of PGA to the 10-formyl derivative occurred. The method cannot be applied directly to crude extracts of natural materials because of the masking effect of nucleotides, amino acids, etc., but should be applicable to material which has been partially purified, e.g., by charcoal adsorption. The sensitivity and specificity of the method might be increased by the use of a biological assay of the eluate fractions.

S. M. MARSH

765. Polarimetric method for the determination of ascorbic acid. G. Nebbia (Ist. Mercegol., Univ. Bologna, Italy). *Acta Vitamin. Milano*, 1958, **12** (3), 107.—The optical activity of ascorbic acid varies from +21° at pH 2.5 to +120° at pH 7. By measurements taken at different pH values the concn. of ascorbic acid can be calculated. N. E.

766. The polarographic determination of vitamin C in fresh fruit and vegetables. S. Krauze and Z. Bozyk (Pharm. Fac., Med. Acad., Warsaw, Poland). *Mitt. Lebensmitt. Hyg.*, Bern, 1959, **50** (4), 228-242.—The influence of various factors (e.g., pH, the nature of the buffer soln., the concn. of HPO_4^{2-} , the type and amount of surface-active material and the presence of O) on the polarographic determination of ascorbic acid is discussed. It is established that, during the reduction process with H_2S , polysulphides were formed as by-products, which have an undesirable influence on the character of the steps of the polarogram and thus accounted for the errors obtained during the titration procedures. The influence of pH in relation to the speed of reduction with H_2S was studied. Dehydroascorbic acid was reduced completely after 15 min. at a pH of 4.7 or 6.2. The results obtained by the polarographic method appear to indicate that no dehydroascorbic acid is present in either fresh fruit or vegetables.

I. DICKINSON

767. Determination of tocopherols in oils, foods and feeding-stuffs. Vitamin-E Panel, Analytical Methods Committee, Society for Analytical Chemistry (14 Belgrave Sq., London). *Analyst*, 1959, **84**, 356-372.—The unsaponifiable fraction of the sample, dissolved in benzene, is passed through a column of floridin earth that has been treated with SnCl_4 and washed with ethanol and benzene, and the column is eluted with benzene. The separation of the tocopherols from the eluate is effected by two-dimensional ascending paper chromatography on paper impregnated with ZnCO_3 and Na fluorescein. The solvent in the first dimension is 30% (v/v) benzene in cyclohexane and in the second dimension 75% aq. ethanol. After the first-dimension chromatography, the paper is immersed in a soln. of liquid paraffin in light petroleum and the solvent is removed by drying. The tocopherols α , δ and ζ separate, β and γ remain together in one spot, and ϵ and η in another. The spots are located either by exposure to u.v. light or by spraying with FeCl_3 and 2:2'-dipyridyl. In the latter method the spots are cut out and the remaining paper is used as a template to locate the spots on a duplicate paper. The cut-out spots are treated with ethanolic soln. of 2:2'-dipyridyl and FeCl_3 , and the extinctions of the soln. are measured at 520 m μ . The method of calculation is given.

A. O. JONES

See also Abstracts—**369.** Determination of alkali metals in molasses. **574.** Separation of carbonyl compounds in flavouring agents. **601.** Determination of *p*-hydroxybenzoic acid esters. **611.** Determination of 5-hydroxymethyl-2-furaldehyde in glucose syrup. **699.** Microbiological assay of vitamins. **791.** Chlorpropham in potatoes. **792.** Aldrin and dieldrin in olive oil.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

768. Spectrographic determination of sodium in atmospheric precipitations. T. K. Zhavoronkina and V. K. Zhavoronkina. *Trudy Morsk. Gidrofiz. Inst., Akad. Nauk SSSR*, 1958, **13**, 143-145; *Ref. Zhur., Khim.*, 1959, (11), Abstr. No. 38,286.—Transfer sample (0.03 ml) with the aid of a pipette to the flat end of the heated lower copper electrode of diam. 2.5 mm, the upper copper electrode being sharpened to a blunt cone, and further heat the electrodes in a special support. Excite the spectra in an a.c. arc with gap 2 mm [the current strength is not given] and photograph them in a glass spectrograph ISP-51 with slit width 0.02 mm and exposure 20 sec. Construct calibration curves of ΔS vs. $\log C$ from the lines Na 5889-9 and Cu 5782-1 Å. The error is $\pm 7.8\%$, and the sensitivity is 0.1 mg per litre.

C. D. KOPKIN

769. Colorimetric determination of sulphur oxides in the atmosphere. S. Kanno. *Intern. J. Air Pollut.*, 1959, **1** (3), 231-233.—Two methods based on the colorimetric reaction between SO_4^{2-} and barium chloranilate are described.

BRIT. COTTON IND. RES. ASS. ABSTR.

770. Spectrophotometric method for the determination of chlorine. Z. Spurný (Inst. Nuclear Res., Czech. Acad. Sci., Prague). *Nature*, 1959, **183**, 1390.—Low concn. of Cl in air and other gases

can be determined by dissolving the Cl in CCl_4 and obtaining the u.v. absorption spectrum of the soln. The max. absorption is at $\approx 335 \text{ m}\mu$ and the peak-height is proportional to the Cl concn., which can be read directly from a calibration curve. The sensitivity is $\approx 2 \times 10^{-8} \text{ M}$ or $1 \mu\text{g}$ per ml. Chlorine dissolved in CHCl_3 , acetone or tri- or tetra-chloroethylene can be determined similarly, but with less sensitivity than with CCl_4 .

W. J. BAKER

771. Photometric determination of mercury [in air]. J. Havránková and J. Volf. *Pracovní Léhářství*, 1958, 10 (3), 250-253.—The method of Ašperger and Murati (cf. *Anal. Abstr.*, 1954, 1, 1789), based on the catalytic effect of Hg^{2+} on the reaction of $\text{K}_4\text{Fe}(\text{CN})_6$ with nitrobenzene to yield a violet colour, was used with good results for the determination of Hg in air. The Hg (0.1 to 200 μg) is separated from interfering ions by electrolysis on a platinum or gold electrode and distillation into chlorine or bromine water.

J. ZÝKA

772. Abundance of nitrous oxide in ground-level air. J. W. Birkeland and J. H. Shaw (Dept. of Physics, Ohio State Univ., Columbus). *J. Opt. Soc. Amer.*, 1959, 49 (6), 637-638.—The concn. of N_2O in air was determined by measuring the absorption of the *P*-branch of the 4.5- μ N_2O band in atmospheric spectra, calibration being effected by means of gas samples containing known amounts of N_2O . The spectra were obtained using a 22-metre multiple-traversed cell, a carbon arc source, and a Perkin-Elmer model-99 double-pass monochromator, with LiF prism and thermocouple detector. The aggregate path length used was 706 metres. The N_2O abundance at Columbus, Ohio, was found to be 0.27 ± 0.05 p.p.m., no variation being detected over a 3-month period. B. S. COOPER

773. Monitoring trace hydrocarbons in air by catalytic oxidation and non-dispersive infra-red analysis. E. J. Rosenbaum, R. W. Adams and H. H. King, jun. (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1959, 31 (6), 1006-1008.—The method is based on the catalytic oxidation of the hydrocarbons to CO_2 , which is measured by i.r. analysis. The limit of detection is < 1 p.p.m. and the calibration curves are linear up to concn. of 300 p.p.m. Known blends of methane in O-N mixtures are used to test the catalyst activity and to calibrate the catalyst and analyser system.

G. P. COOK

774. Bacterial analysis of water by the membrane-filter technique. E. Novel and P. Burkard (Lab. d'Analyse Bactériol., Inst. Hyg., Genève, Switzerland). *Mitt. Lebensmittel Hyg., Bern*, 1959, 50 (3), 188-206 (in French).—The membrane-filter technique has been studied in respect of the influence on the count of *Escherichia coli* of the method of sterilisation of the apparatus, the storage of the sample, the type and method of sterilisation of the membrane, the type of nutrient medium and the time of incubation. The method of sterilisation has no effect on the result. The bacterial suspensions are stable for 3 to 4 hr. at 4° . Lower counts are obtained with MacConkey, eosin methylene blue and deoxycholate media than with the other media examined.

G. BURGER

775. Titrimetric determination of free carbon dioxide in water. O. Thomann and A. Scherer (Kantonalen Chem. Lab., Zürich). *Mitt. Lebensmittel*

Hyg., Bern, 1959, 50 (3), 186-187.—A mixed indicator composed of 0.4% aq. neutralised thymol blue and 0.1% α -naphtholphthalein in 50% aq. ethanol (5:1) gives a better end-point than does phenolphthalein in the titration of CO_2 in water. By matching the green colour at the end-point against that of a buffer soln. at pH 8 to 8.5 containing the same indicator, a precision of ± 1 mg of CO_2 per litre is achieved.

G. BURGER

776. Determination of very small amounts of silicon in water by extraction of an amine salt of silicomolybdenum blue with chloroform, and photometry of the chloroform solution. W. Sonnenschein (Spinnfaser A.-G., Kassel-Bettenhausen). *Z. anal. Chem.*, 1959, 168 (1), 18-28.—To 200 ml of the water under test is added 10 ml of ammonium molybdate soln. [25 g in 100 ml of dil. (1:3) H_2SO_4 plus water to 500 ml] and after 15 min. 5 ml of 10% oxalic acid soln. After a further 5 min. the mixture is treated with 10 ml of reducing soln. (4.1 g of cryst. oxalic acid, 4.0 g of Na formate, 2.12 g of stannous oxalate and 2.4 ml of 98 to 100% formic acid, dissolved in 240 ml of water) and 15 ml of dil. H_2SO_4 (1:3). The mixture is set aside for 10 min. and is then extracted for 3 min. with 10 ml of CHCl_3 , after the addition of 5 ml of amine soln. (5 g of oxyethylated fatty amine, "GCU 20," dissolved in dil. H_2SO_4 to 100 ml). Two more extractions, each with 6 ml of CHCl_3 , are then carried out and the extracts are combined in a flask containing 3 ml of methanol to prevent the development of turbidity. The extract is examined photometrically within 15 min. in a 50-mm cell at 750 μm against pure CHCl_3 , and the silicon is determined by reference to a calibration curve. For 2 μg of SiO_2 per litre the accuracy is within $\pm 10\%$; for greater amounts the accuracy is higher ($\pm 4\%$ at 6.0 μg of SiO_2 per litre). The determination can be carried out in 75 min. and is much more sensitive than previous methods. Because of this sensitivity, water distilled three times in a quartz apparatus is unsuitable for use as a diluent and for the establishment of blank values, and water treated with Amberlite IRA-400 must be used. The method is particularly suitable for the analysis of water poor in silicic acid and for coloured soln.

S. M. MARSH

777. Determination of nitrates in water. I. Procházková (Biol. Fac., Charles' Univ., Prague). *Z. anal. Chem.*, 1959, 167 (4), 254-260.—The reduction of NO_3^- in natural waters to NO_2^- by hydrazine in N NaOH in the presence of a copper catalyst proceeds in 30 min. Any NO_2^- already present are unaffected, and additively determined. Thus NO_2^- can be determined in the presence of NO_3^- . For water with a low NO_3^- content, interfering insol. or macromolecular matter is filtered out by a column of activated charcoal (particle size 0.2 to 0.5 mm) freed from NO_3^- at red heat under CO_2 (for some time) and then de-activated by n -hexane. This enables most of the NO_3^- to be recovered. The NO_2^- in the reduction product are determined as the sulphanilic acid-*l*-naphthylamine complex (extinction at 533 μm), after removal of excess of hydrazine by acetone. The results for 0.01 to 0.4 mg of NO_3^- per litre are accurate to within $\pm 2\%$. Cations that give a ppt. at pH 12.3 may be removed by passage through Wofatit K (Na form). *Procedure*.—Purify the sample if necessary by passage through Wofatit and/or charcoal. To 40 ml of sample add N NaOH (1 ml), keep at 25° for 30 min., and add 1 ml of the reducing soln. (25 ml of 0.48%

hydrazine sulphate and 5 ml of 0.393% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ soln. in 50 ml). Keep at 28° for 30 min. Add acetone (0.5 ml), and after 5 min. add 2.1 ml of 0.3% sulphamic acid in *N* HCl and, after a further 5 min., 1 ml of 0.6% 1-naphthylamine and 1 ml of 27.2% Na acetate trihydrate. Make up to 50 ml and read the extinction at 533 $\mu\mu$ after 15 min. and before 30 min. against a 1-naphthylamine-free blank.

J. P. STERN

778. Determination of orthophosphate, hydrolysable phosphate and total phosphate in surface waters.

Association of American Soap & Glycerine Producers, Inc., Sub-committee on Phosphates. *J. Amer. Wat. Wks Ass.*, 1958, **50** (12), 1563-1574.—The method recommended by this Report is a modification of the isobutyl alcohol technique of Martin and Doty (cf. *Brit. Abstr. C*, 1950, 48). The danger of hydrolysis of condensed phosphate during the determination of orthophosphate is eliminated by reducing the contact time of the sample with acid to 60 to 90 sec. A wet-oxidation method with HClO_4 for total phosphorus is also included. Collaborative analyses by ten laboratories indicated that for synthetic soln. in distilled water the precision was ± 20 to 30% at 0.1 p.p.m., $\pm 10\%$ at 1 p.p.m. and ± 1 to 2% at 20 p.p.m. of P_2O_5 ; for unfiltered surface waters at similar levels of P_2O_5 the precision was approximately halved.

W. T. CARTER

779. Determination of radioactivity in water. U.K.A.E.A. (Res. Group, Woolwich Outstation, C37, Royal Arsenal, Woolwich, London, S.E.18) AERE-AM 51, 1959, 17 pp.—The method is based on AERE C/R 1760 by E. A. C. Crouch and G. B. Cook and is written in its present form by R. G. Osmund and A. G. Pratchett.

780. Determination of uranium and thorium in natural waters after prior enrichment on Amberlite IRA-400 and Dowex 50. P. Korkisch, P. Antal and F. Hecht (Chem. Inst der Univ., Vienna). *Mikrochim. Acta*, 1959, (5), 693-705 (in German).—The two radio-elements U and Th are concurrently concentrated through their ascorbate complexes on the strongly basic anion exchanger Amberlite IRA-400 (ascorbate form). They are subsequently separated from each other and from Ti, Zr, W and Mo by combining the action of this exchanger with that of the strongly acidic cation exchanger Dowex 50 (H^+ form), as well as through the choice of a suitable eluting agent. For U, a polarographic finish is used, with the catalytic nitrate wave; Th is finally determined spectrophotometrically with the aid of thoron. Results from five Bad Gastein springs are reported, and indicate $\simeq 1$ to 12 μg of U per litre and $\simeq 1$ to 13 μg of Th per litre.

D. F. PHILLIPS

781. Determination of benzene in water. F. Devlaminck. *Bull. Cent. Belge Étud. et Docum. Eaux*, 1959, (101), 135-138.—A modification of the colorimetric method developed by Schrenck *et al.* (*U.S. Bur. Mines, Rep. Invest.* No. 3293, 2-1935) is employed. Benzene vapour is removed from the sample acidified with 2 drops of conc. H_2SO_4 by entrainment distillation with nitrogen or air, and nitrated with a freshly prepared mixture of equal volumes of fuming HNO_3 (sp. gr. 1.52) and H_2SO_4 (sp. gr. 1.84). The product is neutralised with NaOH soln. (33%) to phenol red, and extracted with ethyl methyl ketone. The intensity of the colour is measured spectrophotometrically at 560 $\mu\mu$. With the standard apparatus and procedure

described, the maximum sensitivity is 0.01 mg. per litre and the reproducibility is 2% to 5%. The use of acetone in place of ethyl methyl ketone is not recommended since a more complicated extraction procedure is required.

M. G. IVINSON

See also Abstracts—452. Determination of NO_3^- in water. 463. Concn. of Nb in water. 468. Titration of SO_4^{2-} in water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

782. Carotene content of *Ulex europeus* (common furze). D. G. O'Donovan, U. O'Leary and J. Reilly (Dept. of Chem., Univ. Coll., Cork, Eire). *Nature*, 1959, **183**, 1680.—Green prickly spines were separated and blanched in boiling H_2O for 1 min. The samples were treated with acetone - light petroleum (boiling-range 40° to 60°) (3:2) in a high-speed blender with a small baffle plate. The mixture was first neutralised with CaCO_3 , the extract was filtered and the extraction of the residue repeated twice more. The carotene was adsorbed on MgO and Hyflo Super-Cel (1:1), or alumina, eluted with 4% ether in light petroleum, and determined by its u.v. absorption. During the period from Oct. to Feb. or March when furze is fed to stock, the carotene content averages 126 mg per kg. H. F. W. KIRKPATRICK

783. Spectrographic determination of trace elements in soils. P. Mirone and G. Rossi (Ist. Chim. Agrar., Univ. Cattolica del S. Cuore, Piacenza). *Ann. Chim., Roma*, 1959, **49** (2), 306-309.—The method described is based on extraction with 2.5% acetic acid, followed by successive pptn. with 8-hydroxyquinaline, tannic acid, and thionalide. The resulting ppt. is incinerated and placed in the cavity of a graphite electrode, and the spectra are excited in a 5 to 6-amp. d.c. arc, with Ge and Pd as internal standards, and photographed in a quartz spectrograph with a slit-width of 20 μ . Determinations of Ag, Co, Mn, Mo, Ni, Pb, Sn, Ti and Zn in 8 alluvial soils are reported, the amounts ranging from $\simeq 0.005$ to 5 p.p.m.

C. A. FINCH

784. Complexometric determination of extractable iron in soils. P. Fontana and G. Rossi (Ist. Chim. Agrar., Univ. Cattolica del S. Cuore, Piacenza). *Ann. Chim., Roma*, 1959, **49** (2), 310-315.—A complexometric method is described and compared with a modified 1:10-phenanthroline (I) method. Vacuum-dried soil (50 g) is extracted for 2 hr. with 250 ml of a soln. of ammonium acetate (20 g), $(\text{NH}_4)_2\text{SO}_4$ (66 g) and acetic acid (52 g) in water (1 litre); 50 ml of the filtrate is evaporated to dryness, organic matter is destroyed with H_2O_2 , and the residue is treated with HCl (1:2) and made up to 50 ml. Iron in an aliquot of this soln. is determined colorimetrically with a 0.5% soln. of I at pH 3.5 and 490 $\mu\mu$ after reduction of the Fe with quinol. A second aliquot is titrated with a 4% aq. soln. of EDTA (disodium salt), with 1% ethanolic salicylic acid as indicator.

C. A. FINCH

785. [Flame] photometric determination of exchangeable potassium and sodium in soil. G. Gattorta and V. Servello (Staz. Chim.-Agrar. Sper. di Roma). *Ann. Staz. Chim. Agr. Roma*,

1958, Ser. 3, No. 142, 15 pp.—Factors involved in the application of the flame-photometric method to rapid and reproducible routine soil analysis are discussed and a procedure is proposed based on the method of Seay *et al.* (*cf. Brit. Abstr. C*, 1951, 347). *Procedure*—Mix the soil sample (15 g) in a centrifuge tube with a soln. (*A*) (50 ml) containing ammonium acetate (2 N) and ammonium oxalate (0.04 N). Add solid ammonium oxalate (0.5 g) and shake for 30 min. Centrifuge, and transfer the supernatant liquid to a 100-ml flask. Repeat the extraction with *A* (2 x 15 ml), combine the extracts, make up to volume and filter. The photometric readings from this soln. are referred to a standard curve prepared with *A* as solvent.

E. C. APLING

786. Determination of "free" and "available" iron oxides in soils. A. Liani (Cent. Sper. Agric. e Forest. E.N.C.C., Rome). *Ric. Sci.*, 1959, **29** (2), 319-321.—*Procedure*—The soil sample (2 g) is stirred with 10 ml of 0.05 M EDTA (disodium salt) (*I*) at pH 4.3, then centrifuged and filtered; the extraction is repeated. An aliquot of the combined extracts is brought to pH 6 with 2 M Na acetate, and quinol (1% in acetic buffer) and 1:10-phenanthroline hydrochloride soln. (0.5% aq.) are added. A red colour develops after 10 min. and is read by means of a colorimeter or spectrophotometer. The "available" iron is that part immediately utilisable by the soil. When *I* is used at pH 9, slightly lower values are obtained. L. ZANONI

787. Rapid dielectric determination of the residual water content of inorganic fertiliser salts. F. Oehme (Inst. for Development of Anal. Methods, Weilheim/Obb, Germany). *Z. anal. Chem.*, 1959, **187** (4), 271-277.—Determination of the immersion dielectric constant of the powdered salt in water-saturated benzene gives the residual water content of the fertiliser in about 3 min. The apparatus is readily calibrated and the method adequately sensitive. Water contents must be <5%. Water of crystallisation is not determined. J. P. STERN

788. Colorimetric determination of cadmium anthranilate in feeding-stuffs. H. F. Beckman and L. S. Feldman (State Chemist Lab., Texas Agric. Exp. Sta., College Station, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (5), 350-351.—To prepare a standard curve, weigh 2.0 g of a ground blank feed, consisting of a mixture of several types of un-medicated poultry feeds having as great a variety of constituents as possible, into each of six 100-ml flasks, add 0 to 10-ml aliquots of a standard soln. of Cd anthranilate (*I*) (dissolve 0.2 g in 5 ml of conc. HCl and 20 ml of water, and dilute to 100 ml with water; dilute a 10-ml aliquot to 100 ml with water), and dilute to the mark with 1% HCl. Shake occasionally during 30 min., allow coarse particles to settle, filter the supernatant liquid through a layer of Super-Cel with suction, rejecting the first few ml. To 5-ml aliquots of each clear filtrate add 5.0 ml of ethanol, 1.0 ml of HCl soln. (1:1) and 1.0 ml of 0.1% NaNO₂ soln. (prepared fresh daily). Mix well, and after 5 min. add 1.0 ml of 0.5% ammonium sulphamate soln., followed 2 min. later by 1.0 ml of coupling soln. (0.1% aq. soln. of N-1-naphthylethylenediamine dihydrochloride). Heat at 65° for 30 min., cool, and measure the extinctions at 538 m μ . Plot the extinction against concn. of *I*. Treat samples for analysis similarly.

but omit the addition of *I* soln. Recoveries of 100 to 95% were obtained on adding 10 to 15 μ g of *I* to the final aliquot.

S. C. JOLLY

789. Demonstration of lindane [γ -BHC] and a lindane metabolite in plants by paper chromatography. J. P. San Antonio (Crops Res. Div., Agric. Res. Service, U.S. Dept. of Agric., Plant Ind. Sta., Beltsville, Md.). *J. Agric. Food Chem.*, 1959, **7** (5), 322-325.—A semi-quant. method is described for the detection of γ -BHC (*I*) and oil-soluble chlorinated metabolites. The preparation and extraction of *I* from plant material and the purification of the plant extracts before paper chromatography by a modification of the reversed-phase procedure of Mitchell (*J. Ass. Off. Agric. Chem.*, 1954, **37**, 996; 1957, **40**, 294) are discussed. In recovery experiments, in which 100 μ g of *I* was added to the initial plant extracts, 75 to 100% of *I* was recovered.

S. C. JOLLY

790. Analysis of some insecticidal phosphorothioates. E. Sárdi (Inst. for Food Science, Budapest IX, Hungary). *Z. anal. Chem.*, 1959, **187** (4), 241-253.—Column chromatography and subsequent polarography (dropping mercury electrode) are used for the detection and determination of the following analogues of parathion-methyl (*I*)—chlorothion [O-(3-chloro-4-nitrophenyl) OO-dimethyl phosphorothioate] (*II*), isochlorothion [O-(4-chloro-3-nitrophenyl) OO-dimethyl phosphorothioate] (*III*), isomeric chlorothion [O-(2-chloro-4-nitrophenyl) OO-dimethyl phosphorothioate] (*IV*), bromothion [O-(2-bromo-4-nitrophenyl) OO-dimethyl phosphorothioate] (*V*), and para-oxon (diethyl *p*-nitrophenyl phosphate) (*VI*). In ethanol the substances are stable (in the dark) for 5 months, as shown by u.v. spectrophotometry (curves given). Chromatographic separation from impurities is achieved in columns packed with polyethylene, with cyclohexane as stationary phase. The mobile solvent, a pH 4.6 buffer also used for direct polarography, comprises 96% ethanol (10.4 ml), 0.4 M acetic acid (3.0 ml), 0.2 M NaOH (3.0 ml) and 0.15% Tylose (1.0 ml) in 20 ml. At this pH hydrolysis to the corresponding nitrophenol is avoided. Phase-separation occurs overnight. The esters all behave similarly on polarography, and differently from the phenols; the latter have much more negative $E_{1/2}$ values and appear first in the eluate from the chromatographic column. Then follow *VI*, *I*, *II* and *III*, *IV* and *V*, and lastly parathion. Reduction of the ethanol content improves chromatographic separation.

J. P. STERN

791. Determination of isopropyl 3-chlorophenyl-carbamate [CIPC] [chlorpropham] residues in potatoes treated for sprout inhibition. L. N. Gard (Columbia-Southern Chem. Corp., Barberton, Ohio, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (5), 339-341.—The sample of potatoes (200 g) is macerated in a Waring Blender for 3 min. with dichloromethane, and the pulp is removed by centrifuging. The supernatant liquid is evaporated to dryness *in vacuo*, and the residue is heated under reflux with dil. H₂SO₄ to hydrolyse chlorpropham (*I*) to 3-chloroaniline (*II*) and isopropyl alcohol. The soln. is then made alkaline with NaOH and steam-distilled, *II* in the distillate being determined by means of the blue colour produced with ClO⁻ and phenol-NH₂ (Gard and Rudd, *Ibid.*, 1953, **1**,

630). For potato chips, which may contain up to 30% of cooking fat, I in the dichloromethane residue is isolated by extraction with methyl cyanide; the extract is evaporated *in vacuo* and I in the residue is determined by hydrolysis, etc., as described above.

R. E. E.

792. Determination of aldrin and dieldrin residues in olive oil. L. Boniforti and M. Doretti (Ist. Sup. Sanita, Rome, Italy). *R.C. Ist. Sup. Sanit.*, 1959, 22 (2), 189-200.—A preliminary saponification of the oil with ethanolic KOH is followed by extraction with hexane and, after drying, by a further extraction with methyl cyanide. A further extraction is made with hexane from the methyl cyanide phase, after addition of water. The extract is then evaporated almost to dryness. In the presence of aldrin a chromatographic separation is made on a column packed with alumina and silica, which is then eluted with pentane, and the eluate is collected in a glass-stoppered test-tube. The colorimetric procedure is carried out by O'Donnell's method (O'Donnell *et al.*, *J. Agric. Food Chem.*, 1953, 2, 573). In the presence of dieldrin, the sample is reduced with acetic anhydride, HBr and zinc powder, and the colorimetric procedure is carried out as before. The following modifications have been made to O'Donnell's method—(i) the solvent is evaporated at reduced pressure, and (ii) the final coloured soln. is extracted with hexane to eliminate interfering substances from the oil. With the described method 10 p.p.m. of insecticide can be determined in 10 g of oil, and smaller quantities, down to 0.1 p.p.m. or less, in proportionately larger quantities up to 50 g.

L. ZANONI

793. Colorimetric determination of dieldrin in extracts of coffee bark. E. J. Skerrett and E. A. Baker (Res. Sta., Long Ashton, Bristol, England). *Analyst*, 1959, 84, 376-380.—The sample (≈ 10 sq. cm) is extracted in a Soxhlet extractor with benzene, the extract is concentrated to 10 ml, 0.5 g each of CaO and Darco G60 carbon are added, and the mixture is swirled intermittently for 5 min., then poured on to a chromatographic column of alumina surmounted with anhyd. Na_2SO_4 , and the column is eluted with benzene. The eluate is concentrated to 5 ml and treated with a mixture of benzene and boron trifluoride-ether complex (prep. described) at 78° for 30 min., and then cooled to 0°. Saturated NaHCO_3 soln. is added, the cooled liquid is shaken with benzene, the aq. layer is discarded and the benzene layer is washed with water, and dried with Na_2SO_4 . The solvent is removed, and the residue is dissolved in ethanol (0.5 ml) and set aside for 15 min. with 0.1 ml of 2:4-dinitrophenylhydrazine soln. (10 mg in 5 ml of 20% H_2SO_4). Benzene (5 ml) is added and the soln. is washed with HCl, NaOH soln. (10 N), HCl and water, and dried with Na_2SO_4 . The vol. is adjusted with benzene to 7.5 ml, 2.5 ml of ethanol and 1 drop of 25% tetraethylammonium hydroxide soln. are added and, after 1 min., the colour is measured at 440 m μ against the corresponding soln. from uncontaminated bark. Recovery experiments gave good results.

A. O. JONES

See also Abstracts—**396**. Determination of Ca in soil. **452**. Determination of NO_3^- in soil and fertilisers. **757**. Vitamin A in feeding-stuffs. **787**. Tocopherols in feeding-stuffs.

5.—GENERAL TECHNIQUE AND APPARATUS

General

794. Quick-acting chemical balance. B. O. Smith and J. W. Stevens (Physics Dept., British Iron and Steel Res. Ass., London). *J. Sci. Instrum.*, 1959, 36 (5), 206-209.—The displacement of the beam is measured by a displacement transducer, the signal from which is fed to an amplifier. The output current from the amplifier restores the beam to its zero position by means of a moving coil and permanent magnet assembly. The restoring force is directly proportional to this current.

G. SKIRROW

795. Simple burette for drop volumes of 10^{-3} ml. H. Ploum (Max-Planck-Inst. f. Eisenforsch., Düsseldorf). *Z. anal. Chem.*, 1959, 187 (6), 408-410.—The design and operation are described.

E. G. CUMMINS

796. High-precision titrimetry. II. A system of weight titrimetric analysis using arbitrary standards. E. Bishop (Washington Singer Lab., Univ., Exeter, England). *Anal. Chim. Acta*, 1959, 20 (5), 405-412.—The titrimetric procedure described enables the mechanical errors of measurement to be reduced to ≈ 1 in 1×10^6 and the chemical errors to ≈ 1 in 1×10^4 . This is considered to be the max. attainable degree of precision and accuracy in titrimetric processes. The apparatus used consists of a Stanton balance (2 kg), a sealed flask full of liquid (as reference standard), an exactly similar flask containing the sample soln., and a self-lubricating needle-valve weight-burette (described and illustrated). Vacuum corrections are virtually eliminated, adsorption errors are minimised and temp. corrections are unnecessary. Results for titrations of $\text{Na}_2\text{B}_4\text{O}_7$ with HCl, of KI with AgNO_3 , and of As_2O_3 with KBrO_3 are reported. W. J. BAKER

797. Improvements in the determination of the gas content of liquid metals. Brit. Aluminium Co., Ltd. [Inventor: C. E. Ransley]. Brit. Pat. 821,821; date appl. 10.8.54.—The content of H dissolved in a molten metal, e.g., Al, is measured by causing a free surface of the metal to form at a location within the body of the metal (e.g., by immersing a hollow body in the metal), bubbling a small vol. of inert gas (N or A) through the metal below the free surface and circulating it, approx. once per sec. for ≈ 1.5 min., through the metal in a closed circuit extending externally from the body of the metal. The H content of the circulated gas is determined, by means of a katharometer, when it is in equilibrium with the H content of the molten metal.

J. M. JACOBS

798. Apparatus for analysing a liquid for determining the presence therein of carbon dioxide or other substance capable of being liberated in gaseous form. Technicon International Ltd. Brit. Pat. 816,815; date appl. 30.8.57. U.S.A., date appl. 26.9.56.—The quantity of CO_2 in human blood plasma is determined by pumping (by means of rollers acting on resiliently compressible tubing) the plasma and an acid reagent, e.g., dil. H_2SO_4 , in predetermined proportions into a reaction chamber in which the pressure is reduced to form a partial vacuum and achieve a rapid release of the CO_2 . A manometer indicates the rise in pressure resulting

from the liberation of the CO_2 , and thus provides a quant. determination of the CO_2 content of the plasma.

J. M. JACOBS

799. Apparatus for analysing a gas [particularly the alcoholic, acetone or ether content of the human breath]. R. F. Borkenstein. Brit. Pat. 821,013; date appl. 9.1.58.—A measured amount of the gas to be analysed, or the breath of an individual being subjected to a test for alcohol, is passed through a chemical solution [$\text{K}_4\text{Cr}_7\text{O}_7$ in 50% (v/v) H_2SO_4] which is changed in its light-transmitting characteristics by reaction with the gas to be tested. The light transmission is compared photometrically with that of a solution that has not reacted with the gas.

J. M. JACOBS

800. Micro-Kjeldahl digestion apparatus. W. A. Evans, F. B. Johnston and G. M. Ward (Dept. of Agric., Ottawa, Canada). *Lab. Practice*, 1959, **8** (5), 174-175.—The apparatus described and illustrated provides for the digestion of smaller samples (≈ 0.1 g), for a reduction of the digestion time (to ≈ 12 min.), and for an increase in the number of samples (12) that can be handled by one operator. The digestions are made in thick-walled resistance-glass tubes (≈ 30 ml capacity) inserted loosely to a depth of 2 in. into 1-in. holes in a cylindrical aluminium block set on a hot-plate (2000 W, three-heat switch).

W. J. BAKER

801. Apparatus for use in analysing body fluids or the like. Technicon International Ltd. Brit. Pat. 818,023; date appl. 4.3.57. U.S.A., date appl. 23.3.56 and 30.8.56.—Apparatus for analysing liquids that contain crystalloid and non-crystalloid ingredients comprises a dialyser for separating these ingredients, a pump and tubing for feeding the liquids and a processing liquid and air to the dialyser in the form of fluid streams consisting of alternate liquid and air segments, and a colorimeter, with recorder, to which the stream containing the separated crystalloid ingredients is transferred from the dialyser for analysis. A device for blending the liquid segments with each other is interposed in the line between the dialyser and the colorimeter.

J. M. JACOBS

802. Apparatus for counter-current extraction between two liquids. R. Rigamonti (Ist. Chim. Gen. Politecnico, Torino, Italy). *Attual. Lab.*, 1959, **5** (3), 65-70.—A new apparatus for counter-current extraction is described; it is derived from the Craig apparatus, and includes a bulb which permits the displacement of the phase which usually remains stationary.

L. ZANONI

803. Gel filtration: a method for desalting and group separation. J. Porath and P. Flodin (Inst. of Biochem., Univ. of Uppsala, Sweden). *Nature*, 1959, **183**, 1657-1659.—Experiments are described in which dextran gel is used for separating mixtures of substances of sufficient difference in molecular size. A mixture of protein and ammonium sulphate is completely separated by filtration through such a column, elution being carried out with H_2O at a constant rate of 25 ml per hr.

H. F. W. KIRKPATRICK

Chromatography, ion exchange, electrophoresis

804. Chromatographic fraction collector. B. A. Parkin and G. W. Hedrick (U.S. Dept. of Agric., Orlustee, Fla., U.S.A.). *J. Chem. Educ.*, 1959, **36**

(5), 243-244.—The design, construction and operation of a chromatographic fraction collector which takes up to 60 samples are described and illustrated. This cheap and simple apparatus is based on a tipping siphon and is entirely automatic in operation.

O. M. WHITTON

805. Convenient device for the application of spots of test solution to chromatograms. R. Antoszewski (Dept. of Plant Physiol., Univ., Łódź, Poland). *Roczn. Chem.*, 1959, **33** (3), 827-829.—A new simple device for applying spots of liquid to paper chromatograms with simultaneous drying is described. A glass or plastic plate containing a hole of 10 to 30 mm diam. is fixed at a convenient height above a hair dryer. The dryer is switched on, and the paper chromatogram with the starting-point marked is placed on the under surface of the plate, where it is held in position by the stream of air from the dryer. The test liquid is applied through the hole in the plate, and the temp. is controlled by varying the distance of the dryer from the plate. For placing a number of spots on the paper, a plate with a slit (20 mm wide) of the required length is used. The same device can be used for introducing radioactive preparations, not only for chromatographic analysis but also for the measurements of their radioactivity by means of a Geiger counter. The technique described has been found useful in one-dimensional, two-dimensional and radial chromatograms. It ensures a perfectly flat area round the starting-point, thus preventing any slight deformation of the spot.

W. ROUSO

806. Studies on chromatostrips. IX. Effect of the shape of the strips on the R_F value. Tohru Furukawa (Fukuyama Branch of Hiroshima Univ., Hiroshima-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (1), 45-47.—Changes in the R_F value of camphor 2:4-dinitrophenylhydrazone (I) were studied with variously shaped chromatostrips of silica gel cemented with gypsum (Furukawa, *Ibid.*, 1957, **78**, 1185), with hexane-ethyl acetate (17:3) as developer. When the thickness or the width of the strip decreases near the top, the R_F value decreases, whereas when the thickness or the width increases near the top, the R_F value increases. The effect of defects in the strip was also examined. For the separation of terpenes (e.g., α -pinene, limonene and cineole), a strip having a smaller thickness near the top is more suitable.

X. Separation of phenols, aromatic aldehydes, ketones and carboxylic acids with chromatostrips. Tohru Furukawa. *Ibid.*, 1959, **80** (4), 387-389.—In order to eliminate "tailing" of the spots of phenols, aromatic carboxylic acids and 2:4-dinitrophenyl-amino acids on chromatostrips, the use of non-volatile acids for the preparation of the strip was studied. A 0.2 M oxalic acid soln. is the best, the R_F value increasing with increase in concn. (> 0.4 M) of the acid. For the separation of the compounds named, hexane-ethyl acetate (1:1) or benzene is used as developer and conc. H_2SO_4 -conc. HNO_3 (1:1), with or without heating, to locate the spots.

K. SAITO

807. A simple method for the preparation of comparison chromatograms in radial paper chromatography. H. Sulser (Lab. des Eidg. Gesundheitsamtes, Bern, Switzerland). *Mitt. Lebensmittel. Hyg., Bern*, 1959, **50** (4), 287-291.—To enable the development and comparison of two samples to be made on the same paper, a slit of approx. 2 mm

width and 5 to 6 cm length is cut to prevent the two samples from intermixing. The saturated fatty acids and unsaponifiable matter of human milk have been compared with those of cows' milk.

I. DICKINSON

808. Paper-chromatographic front indicators. E. Somfalvy and K. S. Ausch (Plant Res. Stat., Mezőhegyes, Hungary). *J. Chromatography*, 1959, 2 (3), 327-330.—The behaviour of 31 dyes as solvent-front indicators for paper chromatography was investigated. The solvents chosen for study were 12 most commonly used, and both ascending and descending techniques were employed. Results are summarised in a table and indicate that, with Whatman No. 1 filter-paper, for both ascending and descending techniques, dyes such as crystal violet, Rhodamine GGH (C.I. Basic Red 1), Rhodamine ZS, ethanol-soluble Nigrosine (C.I. Acid Black 2), Malachite green (C.I. Basic Green 4), and Sudan III (C.I. Solvent Red 23) are suitable for marking the fronts of nearly all the solvents normally used in paper chromatography.

S. M. MARSH

809. Simple device for R_f determination. H. Berbalk (Inst. f. org. Chem., Tech. Hochschule, Vienna). *Monatsh. Chem.*, 1959, 89, 548-550.—A simply constructed device is described by which the R_f values of paper chromatograms and electro-photograms can be read immediately on a millivoltmeter. The distance travelled by the solvent front can vary between 10 cm and 200 cm. The apparatus consists of a wire on which slides a wire to which is attached a transparent ruler. One end of the wire is fixed and the chromatogram is placed parallel to it so that the starting-point is opposite the fixed end. The ruler is then moved along the wire until it is exactly over the centre of a spot. According to the distance from the starting-point a reading is obtained on a millivoltmeter, and this is compared with a reading taken at the solvent front. Hence the R_f value is calculated.

N. E.

810. New developments in the physical chemistry laboratory. III. Chromatographic ovens. S. Lewin (S.-W. Essex Tech. Coll., London). *Lab. Practice*, 1959, 8 (5), 168-170.—The design of ovens specially suitable for chromatographic drying is discussed and an oven is described which satisfies the requirements for vapour removal, suction, vision, dilution of toxic vapours, temp. and time control, and air filtration and flow. The design and construction of most commercial "chromatographic ovens" are far from satisfactory. A wooden frame which can be fitted into a fume cupboard, to ensure efficient suction over the chromatograms and to obviate the use of a blower-fan, is described.

W. J. BAKER

811. Gas chromatography as a micro-analytical tool. N. Brenner (The Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *Microchem. J.*, 1959, 3 (2), 155-166.—Some of the advantages and limitations of present-day gas chromatography as a micro-analytical technique are discussed and illustrated by an example from the separation of a mixture of esters of fatty acids. A minimum sample range of ≈ 1 to $10 \mu\text{g}$ per component is suggested as a basis for specifying a "proper" sample size for gas chromatography when special techniques (e.g., signal pre-amplification or other "magnifying" devices) are not used. Thus a sample of 1.5 mg is considered to be adequate for gas chromatography, as compared with 10 mg for standard analytical

methods, but most commercial instruments in current use are ill-equipped for the injection of a sample limited to the milligram range. Operating temp. higher than the present max. range of 200° to 300° are desirable to ensure that materials have v.p. > 10 torr in order to pass properly through the column, but this desideratum is limited by the heat stability of the samples. The recently described Golay capillary column ("Gas Chromatography," Coates, Noebels and Fagerson, Academic Press, New York, 1958) should result in "order of magnitude" gains in the performance and latitude of instruments, and permit of a 1000-fold decrease in sample size. The ionisation gauge detectors of McWilliam and Dewar (cf. *Anal. Abstr.*, 1958, 5, 4364) and of Lovelock (cf. *Anal. Abstr.*, 1958, 5, 3208) are further developments ideally suited to the requirements of the Golay column system and theoretically enable 10^{-18} and 10^{-19} g of component gases to be measured, respectively. These developments increase the problems of the qual. identification of sample components by standard laboratory means, but it is suggested that the high resolving power of the capillary system may eventually result in identification based solely on retention characteristics.

D. F. PHILLIPS

812. Analysis by gas chromatography of a "pure" sample with an "impure" carrier. V. Willis (Instrument Devel. Sect., I.C.I. Ltd., Billingham Div., Co. Durham). *Nature*, 1959, 183, 1754.—In the case of the analysis of a gas containing impurities no carrier gas of greater purity was available. The same gas containing the same impurities in higher concn. was therefore used as carrier, deficiencies of components being recorded as negative peaks in the chromatogram. The calibrations, checked by mass spectrometry, are approx. the same for negative and positive peaks.

A. R. ROGERS

813. Gas chromatography. Application to the study of rapid degradative reactions in solids. S. B. Martin (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *J. Chromatography*, 1959, 2 (3), 272-283.—Specialised gas-chromatographic techniques are described for analysing the products evolved when organic solids, or liquids with low vapour pressure, are pyrolysed rapidly by radiant energy. The exposure apparatus is illustrated and comprises an exposure chamber, cold traps and a gas-solid chromatographic column for analysing uncondensed gases. A by-pass round the cold traps is provided to divert the carrier gas directly to the column, so that while the uncondensable products are passing through the column no condensed material is carried over. The condensable products are removed from the cold traps and analysed by other gas-solid adsorption and gas-liquid partition chromatographic columns. The possibility of the occlusion of uncondensable products in the condensates is overcome by repeatedly vapourising and re-condensing the condensates in a sealed trap. The possibility of overlooking a substance which is not retained by the cold trap, and for which the column packing is not a suitable partition medium, is avoided by repeating the experiment with different combinations of cold-trap media and column packing. Typical combinations together with the separations given are tabulated. Full operating details are given. The apparatus has so far only been applied to the study of the pyrolysis products obtained from α -cellulose.

S. M. MARSH

814. Ionisation chamber for high-temperature gas chromatography. L. H. Mason, H. J. Dutton and L. R. Bair (N. Utilization Res. and Dev. Div., Agric. Res. Service, U.S. Dept. Agric., Peoria, Ill., U.S.A.). *J. Chromatography*, 1959, **2** (3), 322-323.—Full constructional details are given of an ionisation chamber suitable for monitoring radioactive compounds during gas chromatography at high temperature (to 240°). The main construction material is Teflon and the chamber is lagged with Pyrex-glass wool. A chromatogram obtained for tritium-labelled methyl stearate chromatographed on a Resoflex-296 column at 205° with a He flow-rate of 44 ml per min. is presented. Radioactivity measurement lags about 20 sec. behind thermal-conductivity measurements. It is evident that tritium-labelled methyl stearate is chromatographically identical with inactive stearate. Some labile tritium contaminant is present.

S. M. MARSH

815. Nylon capillary columns for use in gas-liquid chromatography. R. P. W. Scott (Res. Sect., Benzoile Producers Ltd., Watford, Herts, England). *Nature*, 1959, **183**, 1753-1754.—A nylon capillary, 1000 ft. \times 0.02 in., coated internally with dinonyl phthalate, has been used for the separation of paraffin hydrocarbons. At 20° to 23°, this column showed an efficiency of 750,000 theoretical plates for butane, which was eluted in \approx 60 min. For *n*-hexane and *n*-heptane the corresponding figures were, respectively, 500,000 and 90 min., and 250,000 and 170 min.

A. R. ROGERS

816. Polyester liquid phases in gas-liquid chromatography. E. C. Horning, E. A. Moscatelli and C. C. Sweeley (Lab. of Chem. of Natural Prod., Nat. Inst. of Health, Bethesda, Md., U.S.A.). *Chem. & Ind.*, 1959, (25), 751-752.—A procedure is described for coating Celite with a polyester for use as the stationary phase in the chromatography of methyl esters of fatty acids. The Celite is treated with dichlorodimethylsilane in the vapour phase in nitrogen, and then with methanol according to the procedure described by Howard and Martin (*Biochem. J.*, 1950, **48**, 532). The treated Celite is stirred with a soln. of polyester in acetone, filtered off and dried at 110°. Polymers prepared from succinic acid or glutaric acid with diethylene glycol were particularly efficient for separating samples of biological origin, e.g., stearates and oleates.

G. BURGER

817. Selectivity of the liquid phase in gas chromatography and the choice of supporting medium. E. Bayer (Inst. f. Org. Chem. der T. H., Karlsruhe). *Angew. Chem.*, 1959, **71** (9), 299-302.—The log of retention volume plotted against boiling-point for groups of compounds (e.g., normal paraffins, olefins and cyclic paraffins) for various liquid phases used in gas chromatography give families of straight lines, the relative slopes and positions of which depend on the liquid medium. The "selectivity constant" is defined as the ratio of retention volume for two compounds of the same b.p. in the two classes it is desired to separate. Values are given for 7 liquid media for 8 classes of hydrocarbon, together with selected values for 16 other systems. The relative merits of kieselguhr and ground fireclay as supporting media are discussed.

T. R. ANDREW

818. Use of katharometers in gas chromatography. M. Eden, A. Karmen and J. L. Stephenson (Lab. of Tech. Devel., Nat. Heart Inst., Bethesda, Md., U.S.A.). *Nature*, 1959, **183**, 1322.—The equation derived by Ray (*Ibid.*, 1958, **182**, 1663) for the sensitivity of a katharometer [$dt/dx = -a(k_1 - k_2)/k_1^2$] led to the conclusion that the carrier gas of lowest thermal conductivity would give the highest sensitivity. This conclusion is not of general application. The katharometer response may be positive or negative, depending on whether the organic vapour being detected has $k_2 < k_1$ or $k_2 > k_1$, respectively, and the amount of response varies greatly. In any case, the function derived by Ray has a max. when $k_1 = 2k_2$. Further, it is common practice when a gas of higher thermal conductivity is used as carrier to increase the current so that the temp. difference between the hot wire and cell wall is kept constant; then $dt/dx = -a(k_2 - k_1)/k_1$. In this case He is superior to both A and N.

J. H. WATON

819. Effect of carrier gas on katharometer response. W. A. Wiseman (Gas Chromatography Ltd., 176 Old Brompton Rd., London). *Nature*, 1959, **183**, 1321-1322.—In considering the heat balance of a katharometer, the heat loss is not negligible. On neglecting this term for H and He, the response of a katharometer at constant temp. should be inversely proportional to the square root of the thermal conductivity of the carrier gas. When the eluted gas has a very much lower thermal conductivity than the carrier gas, the terms $(k_1 - k_2)/k_1$ must be qualified by the introduction of constants to give $(b_1 k_1 - b_2 k_2)/k_1$, where b_1 and b_2 are only approx. unity.

J. H. WATON

820. Effect of the carrier gas on the sensitivity of thermal-conductivity detectors in gas chromatography. B. A. Scott and A. G. Williamson (Dept. of Chem., Univ. of Calif., Los Angeles, U.S.A.). *Nature*, 1959, **183**, 1322-1323.—Some disadvantages of the use of a carrier gas of low thermal conductivity, e.g., A, are pointed out. Sensitivities varying from large positive values through zero to large negative values are found, whereas with He the sensitivity is more or less constant. When the thermal conductivity of the eluted material is equal to that of the carrier gas (at the effective temp.), then the detector is insensitive. It would seem, particularly for unknown gases, that it is preferable to use He or H as carrier gas rather than one of low thermal conductivity, except in cases when calibration has shown that the ultimate sensitivity is substantially higher.

J. H. WATON

821. Physico-chemical methods for the determination of optimum conditions in paper electrophoresis. W. Croon and H. Croon (Staatl. Inst. f. Hygiene u. Infektionskrankheiten, Saarbrücken). *Z. anal. Chem.*, 1959, **188** (2), 115-119.—A study of the effect of various factors on the electrophoresis of protein soln. is described. Electrophoresis with stabilised current enables higher voltages to be used without the necessity for cooling, and reduces the time required for the separation by about one-third. The best separation is achieved under alkaline conditions, and the distance travelled by the proteins increases as the conductivity of the buffer is reduced. A method for enriching dilute protein soln. is described which involves evaporation from the paper in an open chamber which is heated

electrically. Concentration is obtained in about 3 hr. and the mixture can be separated on the same strip by subsequent electrophoresis.

S. M. MARSH

822. Ionophoretic pattern in two-dimensional electrophoresis. H. Peeters, P. Vuylsteke and R. Noë (St. Jans Hospital, Bruges, Belgium). *J. Chromatography*, 1959, **2** (3), 308-319.—Details are given of an apparatus which has been used to study the effects of evaporation and of ionophoresis in two-dimensional electrophoresis. It has been found that there is no evaporation in a horizontal direction if the equilibration time is sufficiently long (about 6 hr.), but in a vertical direction there is evaporation towards the bottom. Studies of ionophoretic effects were made with (i) a single buffer of Na or K barbitone, (ii) Na and K barbitone buffers of the same ionic strength simultaneously and (iii) Na, Li and K barbitone buffers simultaneously. Results are described fully for the three series of experiments. A characteristic distribution of electrolytes occurs with an accumulation in the para-anodic region which causes differences in the conductivity of the paper. The observations are discussed theoretically.

S. M. MARSH

823. Electrophoresis on a separable column. E. Panconesi and G. Mantellassi (Univ., Florence, Italy). *Sperimentale*, 1958, **108**, 338-349.—Filter-paper discs are soaked in buffer soln. and packed as a column connected at both ends, by means of feeder tubes filled with cotton, to glass cells containing buffer, and electrode compartments. Several discs are soaked in a test fluid (serum) and inserted near the cathodic end. A good separation is obtained within 20 to 25 hr. with a potential of 400 to 600 V, 30 to 35 mA and an ionic strength of 0.01. The fractions are located by staining and measured with a photo-electric densitometer. When a fraction is needed for further use, half of the disc is stained and the other half used.

CHEM. ABSTR.

Optical

824. Monitored Geiger-counter X-ray diffractometer with automatic recording. E. R. Pike and J. W. Hughes (Viriamu Jones Lab., Univ. Coll., Cardiff). *J. Sci. Instrum.*, 1959, **36** (5), 212-223.—The diffraction pattern is scanned in steps of 0.02° (2θ) with a Geiger counter as detector. Dekatron decade scalers are used for indicating both the monitor counts and those from the specimen detector on the diffractometer. The readings from the specimen detector scaler and those of the angular position indicator are automatically recorded on micro-film. Electronic circuits are described.

G. SKIRROW

825. Apparatus for porous-cup spark analysis. O. E. Clinton (Rukuhia Soil Res. Sta., Dept. of Agric., Hamilton, N.Z.). *Spectrochim. Acta*, 1959, (3-4), 283-286.—A description is given of a two-position electrode stand which enables loading and sparking operations to be carried out at the same time. An automatic exposure timer and plate-racking mechanism are incorporated.

P. T. BEALE

826. Simple cup-electrode for spectrographic analysis of solutions. G. P. Mitchell, G. Orme and F. Farrell (Mullard Radio Valve Co., Ltd., New Rd., Mitcham Junc., Surrey, England). *Spectrochim.*

Acta, 1959, (3-4), 272-274.—The graphite electrode is of the porous-cup type, but has a base 0.1875 in. thick, which is untreated. The cup is inverted over the end of a 0.125-in. tungsten rod, which is sealed into the neck of a funnel-shaped glass reservoir. The graphite protrudes 1 mm above the mouth of the glass cup, which is filled to the brim with the solution to be excited. Two sizes of reservoir of capacity 2 ml and 6 ml have been used. Arc-like multisource discharges may be passed to give high sensitivity without appreciable sputtering of the soln. The technique has been applied to the analysis of nickel alloys, for which the quant. limit of estimation is $\approx 0.005\%$ for Si, Mn, Co, Cu, Fe, Cr and Mg.

P. T. BEALE

827. Evaluation of calibration data with reference to the variable internal standard method. A. B. Calder (Haydon House, Fairfield Rd., Stockton-on-Tees, Co. Durham). *Spectrochim. Acta*, 1959, (3-4), 280-283.—The well-known spectrographic methods of Scott (*J. Soc. Chem. Ind.*, 1946, **65**, 291) and Mitchell ("Spectrographic Analysis of Soils, Plants and Related Materials," Commonwealth Agric. Bureau, Tech. Comm. No. 44, 1948) for the analysis of concentrates, soils, etc., by using known additions of Fe_2O_3 as the variable internal standard, may be shortened (only 24 spectrograms are required instead of 72), and the calculations simplified, by consideration of the statistical principles involved.

P. T. BEALE

828. Application of time resolution to a spectrographic source. C. A. Baker [U.K.A.E.A. (Res. Group), Woolwich Outstation, Royal Arsenal, London]. A.E.R.E. Report AERE-R 2926, 1959, 10 pp.—An optical apparatus is described that can resolve the repetitive discharge of a spectrographic excitation source into 10-μsec. intervals. Time-resolved spectra have been obtained with a triggered low-voltage a.c. arc, the discharge from which is variable in character over a wide range from 300 to 2000 μsec. Analytically, the use of time-resolved spectra may aid (i) in selecting the best line pairs; (ii) in reducing or eliminating the background by removing the early part of a discharge which gives rise to a continuum; (iii) in selecting the part of a discharge where the line required reaches max. intensity; and (iv) in improving reproducibility by allowing lines to be selected which are not subject to reversal, or by the use of the part of the discharge where such lines are not reversed.

K. A. PROCTOR

829. Improvements in or relating to apparatus for making spectral analysis [of pulverised materials]. N. A. Danielsson. Brit. Pat. 821,849; date appl. 3.4.56. Sweden, date appl. 31.3.55.—The powdered material is distributed in an even layer on a web provided with an adhesive surface, e.g., an adhesive tape. The tape is caused to travel between a pair of electrodes between which sparks are discharged at intervals, and means are provided for receiving the light emitted from the sparks for spectral analysis.

J. M. JACOBS

830. Micro-spectrophotometer for u.v. and visible spectra. A. Catino, A. Ceruti and J. Colombino. *Attual. Lab.*, 1959, **5** (3), 73-84.—The apparatus described comprises a microscope and a spectrophotometer and permits spectra to be obtained on very small samples ($\approx 10^4$ times smaller than those required by ordinary spectrophotometers). With

this apparatus solid samples can be examined, e.g., single fibres, small crystals and tissues.

L. ZANONI

831. A photo-electric densitometer. H. Perperot. *Ann. Falsif.*, 1959, **52**, 226-228.—A description is given of a direct-reading absorptiometer in which a selenium barrier-cell is used. E. J. H. BIRCH

832. Apparatus for spectrophotometric microtitration. Application to the titration of deuterohaemin. A. C. Maehly and V. Legallais (The Johnson Foundn. for Med. Physics, Univ. of Pennsylvania, Philadelphia). *Experientia*, 1959, **15** (5), 198-199 (in English).—A small attachment for a Beckman spectrophotometer is described which allows concomitant measurement of the extinction and pH. The assembly has been used for titrating de-allyl-protohaemin IX (deuterohaemin). The *K* value was found to be 6.8 ± 0.05 .

P. NICHOLLS

833. Infra-red vacuum spectrometer with prism/grating double monochromator. C. S. C. Tarbet and E. F. Daly (Unicam Instruments Ltd., Cambridge, England). *J. Opt. Soc. Amer.*, 1959, **49** (6), 603-608.—The instrument described may be used either as a single prism monochromator or as a prism/grating double monochromator with a choice of two replica gratings to cover the spectral ranges of 650 to 2150 cm^{-1} and 2150 to 3650 cm^{-1} , respectively. The resolution is 0.3 cm^{-1} at 950 cm^{-1} . Magnetically operated slits provide constant energy background. The whole instrument can be evacuated to a working pressure of 10^{-3} torr.

B. S. COOPER

834. Infra-red absorptiometer, using interference filters, for analysis of hydrogen fluoride in gaseous mixtures. J. A. Harrison and C. D. Reid (U.K.A.E.A. (Ind. Group), Res. & Dev. Branch, Capenhurst, Cheshire). *J. Sci. Instrum.*, 1959, **36** (5), 240-242.—A wavelength-scanning i.r. absorptiometer for use with corrosive gas mixtures is described. Scanning is achieved by oscillating an interference filter at 10 c/s , thus passing alternate beams of different wavelength through the sample tube. One beam is absorbed while the other serves as a reference beam. The calibration is independent of window corrosion in the absorption tube. The instrument will detect partial pressures of hydrogen fluoride in the range 0.02 to 20 torr in 1 atm . of mixture.

G. SKIRROW

835. Versatile apparatus for automatic recording of absolute fluorescent spectra. F. R. Lipsett (Div. Radio and Electrical Engng, Nat. Res. Council, Ottawa 2, Canada). *J. Opt. Soc. Amer.*, 1959, **49** (7), 673-679.—Ultra-violet light is dispersed by a grating monochromator and focused on a specimen. Fluorescent light from the specimen passes through a second monochromator and is detected by a photomultiplier. The spectral sensitivity characteristics of the detecting photomultiplier together with its associated monochromator and mirrors are corrected by means of a cam driven in synchronism with the wavelength drive of the detecting monochromator. The optical system is calibrated photometrically by means of a standardised tungsten-quartz lamp. In order to cancel fluctuations in the exciting light source, a fraction of the light emerging from the source monochromator is focused on to a second photomultiplier, whose out-

put is used to operate a servo system. The recorded spectrum is thus a measure of the ratio of fluorescent to exciting light.

N. E.

836. Fluorescent-indicator adsorption analysis using the chromanalyser. J. G. Allen and J. C. S. Wood (Sun Oil Co., Toledo, Ohio, U.S.A.). *Bull. A.S.T.M.*, 1959, (238), 49-52.—A new apparatus is described to replace the standard equipment for the separation and determination of olefins, and aromatic and saturated hydrocarbons in petroleum products by the fluorescent-indicator adsorption method of Criddle and LeTourneau (*Anal. Chem.*, 1951, **23**, 1621). The chromanalyser can be operated on the bench under normal lighting, whilst the silica-gel columns are now shorter and stronger. Values obtained for both high and low contents of aromatics and olefins are within $\approx 2\%$ of those obtained by the acid treatment-bromine number method. With the eight columns about 24 samples can be analysed per day.

W. J. BAKER

837. Illuminant for the colorimetry of fluorescent materials. W. Harrison (Station Rd., Midge Hall, nr. Preston, Lancs., England). *J. Sci. Instrum.*, 1959, **36** (5), 234-236.—The illumination of fluorescent whitening agents requires a source having an adequate u.v. content. The use of two supplementary sources is suggested, one being equivalent to Illuminant C (a filament lamp at 3000°K , screened with a Chance O.B.8 filter), the other the same lamp screened with a Chance O.X.1 filter.

G. SKIRROW

838. X-ray spectrograph as modified by Cauchois, adapted for use with a Geiger-Müller counter. V. Miron. *An. Stiint. Univ. "Al. I. Cuza" din Iasi*, 1958, **4** (2), 105-118.—The Cauchois method, in which a curved mica crystal is used, is modified by mounting four crystals on a rotating cylinder so that each can be used independently. The photographic unit can be replaced with other recording devices, e.g., a Geiger counter. It is claimed that, by combining the Cauchois method with that of St. Procopiu, which is based on the use of a Geiger counter with a galvanometer, the recording of some spectral lines takes only 45 sec. compared with the 5 hr. required for the photographic method.

H. SHER

839. X-ray absorption coefficients and geometrical collimation of the beam. L. G. Parratt, J. O. Porteus, H. W. Schnopper and T. Watanabe (Cornell Univ., Ithaca, N.Y.). *Rev. Sci. Instrum.*, 1959, **30** (5), 344-347.—A high-resolving-power monochromator is commonly used to provide high angular collimation of an intense X-ray beam for the measurement of absorption coeff. The effect of the absorber position, relative to the monochromator, on the coeff. when the absorber exhibits small-angle scattering of significant intensity in a scattering cone as large as a few seconds of arc, is discussed, with examples.

P. T. BEALE

Electrical

840. Effect of gelatin and polyoxyethylene lauryl ether on polarographic diffusion currents of inorganic ions. Reita Tamamushi, Satomi Yamamoto, Akiko Takahashi and Nobuyuki Tanaka (Univ. Tohoku, Sendai, Japan). *Anal. Chim. Acta*, 1959,

20 (5), 486-493.—Gelatin in concn. $>0.05\%$ generally decreases the diffusion current constant (k) of bivalent metals (Cu, Pb, Co, Zn, Cd) at the dropping mercury electrode, whereas polyoxyethylene lauryl ether (I) at all concn. between 10^{-6} and 10^{-3} M is without effect on k . The max. suppression points of I are usually $<10^{-4}\text{ M}$, and this stable compound (or a similar synthetic detergent) is strongly recommended as a max. suppressor in polarographic analyses of high sensitivity. **W. J. BAKER**

841. Laboratory potentiometric pH meters. British Standards Institution (2 Park Street, London, W.1.). B.S. 3145:1959, 7 pp.—The essential performance requirements of meters for general laboratory use are specified.

842. Chronopotentiometry. Simultaneous analysis of multiple constituents. Y. Takemori, T. Kambara and I. Tachi (Univ., Kyoto, Japan). *Z. phys. Chem.*, 1958, 89-96.—A graphical method is described by which the analysis can be accomplished by means of a curve of stepped potential *vs.* time. The basis of the method is explained in a generalised theoretical treatment of the chronopotentiometric electrolysis of a soln. containing any desired concn. of several depolarising materials having different reduction potentials. The application of the method is illustrated by the analysis of soln. containing Ti^{4+} , Cd^{2+} and Zn^{2+} . **CHEM. ABSTR.**

843. Sub-microgram-scale analysis by coulometry at controlled potential. L. Meites (Polytech. Inst., Brooklyn, N.Y., U.S.A.). *Anal. Chim. Acta*, 1959, **20** (5), 456-462.—Methods of ensuring max. accuracy when determining sub-microgram amounts of, *e.g.*, Zn, by controlled-potential coulometry are discussed. The ultimate sensitivity depends on the accuracy with which the background corrections, especially that for the charging quantity of electricity, can be determined. Max. sensitivity and accuracy are secured when the final current integration is made during a very rapid electrolysis requiring only a very small continuous faradaic current. A method for the coulometric determination of Zn based on these principles has a limiting uncertainty of $\pm 0.2\text{ m}\mu\text{F}$, so that as little as $0.07\text{ }\mu\text{g}$ of Zn can be determined to within $\pm 10\%$ and amounts $>10\text{ }\mu\text{g}$ to within $\pm 0.1\%$. Possible procedures for extending controlled-potential coulometry into the millimicrogram range are indicated. **W. J. BAKER**

844. Scintillation counter method of intercomparing neutron source strengths by means of a manganese sulphate bath. E. R. Mosburg, jun. *J. Res. Nat. Bur. Stand.*, 1959, **62** (5), 189-191.—The substitution of a sodium iodide scintillation counter for a Geiger-Müller counter in a bath of MnSO_4 soln. (1 metre depth \times 1 metre diam.) makes possible the calibration of sources weaker by a factor of seven. High stability of the measuring system was achieved by maintaining equal count rates in the two channels of a differential pulse height analyser with the channels set symmetrically about the photopeak of a standard source of ^{137}Cs - ^{137}Ba . **G. J. HUNTER**

845. Contribution of nuclear emulsions to the study of some cases of micro-radiochemistry. G. Mayr (Fac. Med., Univ. di Milano, Italy). *Ric. Sci.*, 1959, **29** (4), 804-809.—A method is described, based on the count of the terminal parts of β -ray tracks in nuclear emulsions, for determining the amount of a β -ray emitter even when the rays are highly energised. A second method is also described, based on the same principle, for the determination of small amounts of a β -emitting isotope in a mixture with another isotope emitting β -rays of higher energy. **L. ZANONI**

846. High-resolution nuclear resonance apparatus. J. B. Leane, R. E. Richards and T. P. Schaefer (Phys. Chem. Lab., Oxford). *J. Sci. Instrum.*, 1959, **36** (5), 230-233.—A nuclear resonance spectrometer is described which has a resolving power of approx. 1 in 10^8 with samples of 5 mm diam. A thermally lagged permanent magnet is used to provide the main field, and the spectrometer is a simple bridged-T type. **G. SKIRROW**

847. Radio-assay of aqueous solutions mixed with solid crystalline fluors. D. Steinberg (Lab. of Cellular Physiol. and Metab., Nat. Heart Inst., Bethesda, Md., U.S.A.). *Nature*, 1959, **183**, 1253-1254.—In the direct radio-assay of aq. soln. of weak β -ray emitting isotopes by liquid scintillation spectrometry (*Ibid.*, 1958, **182**, 740), the plastic into which the fluor is incorporated can be substituted by a number of less expensive, more efficient and more generally available crystalline fluors, of which blue-violet fluorescence-grade anthracene crystals give the best result. The method can be applied to any material soluble in aq. solvents and not reacting with anthracene, and to the counting of material of low specific activity when large amounts are available. **K. A. PROCTOR**

THE QUÉRE TITRATOR

has wide applications in
recording physico-chemical processes

The Quéré Titrator is a precision instrument for recording titrations accurately. Equipped with an automatically variable recording table to suit the gradient of the curve, it permits the rate of advance to be reduced when the rate of change increases. Reagent flow is controlled by the table mechanism and by changing the jet of the syringe, the volume being represented by the abscissa of the graph and the state of mixture by the ordinate. The circle method determines accurately the end points of titration. *The circuits permit all kinds of potentiometric titrations and with special attachments it is possible to perform conductimetric or polarised-electrode titrations.*



- * **PHOTOMETRY** The Quéré strip photometer attachment is provided with filters and a vacuum type photocell giving accurate and stable readings.
- * **USING A LIQUID MEDIUM** photometric attachment to this Recorder allows any photocolorimetric titration, recording photometric variations instead of equivalent points.
- * **INTEGRATION** The Recorder automatically integrates the curve as it is traced. The results are entered on the axis of the ordinate of the curve by means of an electric pen marking 'tens' and 'units'.
- * **RECORDING TIME FUNCTIONS** The Titrator is fitted with a zero drift correcting circuit using an automatic potentiometer. To make accurate measurements it is necessary only to check the zero periodically; the instrument itself will then introduce the necessary corrections.

Write for fully illustrated and descriptive leaflet

Tinsley

H. TINSLEY & CO. LTD.

Werndee Hall, South Norwood, London, S.E.25
Tel: ADDISCOMBE 6046-8

JSP 5719

Routine Values

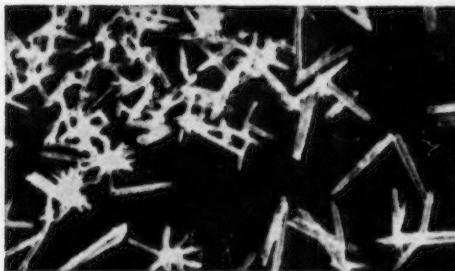
a concept of importance for all research workers

The concept signifies a painstaking empiricism, the thorough regard for routine detail, those less dramatic aspects of research. Concern for "routine values" covers many things, from the design of apparatus to the quality of research materials. It is as relevant in the development of papers for filtration as to work in any other branch of science or technology.

Applied for more than a century, the concept has set a seal of excellence on every Whatman Filter Paper.

The result is that *Whatman* has come to stand for the most reliable range of filter papers. They are an automatic choice of research organisations in Great Britain and in many other countries. They bring a consistently high standard of performance—a routine *Whatman* feature—to all filtration procedures.

The range of *Whatman* Filter Papers is discussed in the "Filtration Section" of the *Whatman* catalogue. Please write for a copy of this monograph and of the *Whatman* "Buyers' Guide."



H. REEVE ANGEL & CO LTD

GT. BRITAIN 9 Bridewell Place London EC4
U.S.A. 9 Bridewell Place Clifton New Jersey

The photograph shows crystals of Vitamin B₁₂, the anti-pernicious anaemia factor isolated by Glaxo Laboratories Ltd. In their Research Division Glaxo use *Whatman* Papers for routine filtration, as well as for chromatography and electrophoresis.



Sole distributors of

WHATMAN FILTER PAPERS

manufacturers W. & R. Balston Ltd.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	.	a.c.	milli-equivalent	.	milli-equiv.
ampere	.	amp.	milligram	.	mg
Ångström unit	.	Å	millilitre	.	ml
anhydrous	.	anhyd.	millimetre	.	mm
approximate, -ly	.	approx.	millimicrogram	.	$m\mu g$
aqueous	.	aq.	millimolar	.	mM
atmospher-e, -ic	.	atm.	millivolt	.	mV
boiling-point	.	b.p.	minute (time)	.	min.
British thermal unit	.	B.Th.U.	molar (concentration)	.	M
calorie (large)	.	kg.cal.	molecul-e, -ar	.	mol.
calorie (small)	.	g.cal.	normal (concentration)	.	N
centimetre	.	cm	optical rotation	.	α
coefficient	.	coeff.	ounce	.	oz
Colour Index	.	C.I.	parts per million	.	p.p.m.
concentrated	.	conc.	per cent.	.	$\%$
concentration	.	concn.	per cent. (vol. in vol.)	.	$\%$ (v/v)
constant	.	const.	per cent. (wt. in vol.)	.	$\%$ (w/v)
crystalline	.	cryst.	per cent. (wt. in wt.)	.	$\%$ (w/w)
crystallised	.		potential difference	.	p.d.
cubic	.	cu.	precipitate (as a noun)	.	ppt.
current density	.	c.d.	precipitated	.	pptd.
cycles per second	.	c/s	precipitating	.	pptg.
density	.	ρ	precipitation	.	pptn.
density, relative	.	d or wt. per ml	preparation	.	prep.
dilute	.	dil.	qualitative, -ly	.	qual.
direct current	.	d.c.	quantitative, -ly	.	quant.
distilled	.	dist.	recrystallised	.	recryst.
ethylenediaminetetra-acetic acid	.	EDTA	refractive index	.	n^a
electromotive force	.	e.m.f.	relative band speed	.	R_F
equivalent	.	equiv.	relative humidity	.	r.h.
gram	.	g	revolutions per minute	.	r.p.m.
gram-molecule	.	mole	saponification value	.	sap. val.
half-wave potential	.	$E_{\frac{1}{2}}$	saturated calomel electrode	.	S.C.E.
hour	.	hr.	second (time)	.	sec.
hydrogen ion exponent	.	pH	soluble	.	sol.
infra-red	.	i.r.	solution	.	soln.
insoluble	.	insol.	specific gravity	.	sp. gr.
international unit	.	i.u.	specific rotation	.	$[\alpha]^a$
kilogram	.	kg	square centimetre	.	sq. cm.
kilovolt	.	kV	standard temp. and pressure	.	s.t.p.
kilowatt	.	kW	temperature	.	temp.
liquid	.	liq.	ultra-violet	.	u.v.
maxim-um, -a	.	max.	vapour density	.	v.d.
melting-point	.	m.p.	vapour pressure	.	v.p.
microgram	.	μg (not γ)	volt	.	V
microlitre	.	μl	volume	.	vol.
micromole	.	μ mole	watt	.	W
micron	.	μ	wavelength	.	λ
milliampere	.	mA	weight	.	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	.	.	>	less than	.	.	<
not greater than	.	.	\geq	not less than	.	.	\leq
is proportional to	.	.	\propto	of the order of, approximately	.	.	\approx

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II} , Mo^{V} . Substances in the ionic state are represented by Na^+ , Fe^{3+} , Fe^{2+} , etc., for cations and by Cl^- , SO_4^{2-} , PO_4^{3-} , etc., for anions.

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: B. A. Ellis

Members: B. S. Cooper, C. H. R. Gentry, C. A. Johnson, H. F. W. Kirkpatrick, B. J. Walby, W. A. Waygood, K. A. Williams and

President of the Society: R. C. Chirnside

Hon. Secretary of the Society:
R. E. Stuckey

Hon. Treasurer of the Society:
A. J. Ames

Editor: Norman Evers, B.Sc., Ph.D., F.R.S.C.

Assistant Editor: Mrs. H. J. Fisk, B.Sc.

CONTENTS

Printed and published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England.
Communications to be addressed to the Editor, Norman Evers, 14, Belgrave Square, London, S.W.1.
Enquiries about advertisements should be addressed to Walter Judd Ltd., 17, Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office.

